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THESIS

# MODIFICATION OF SOME PROPERTIES OF CELLULOSE BY ALTERNATE WETTING AND DRYING

by

Alex Rosenthal

Edmonton, Alberta. April, 1949.

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# MODIFICATION OF SOME PROPERTIES OF CELLULOSE BY ALTERNATE WETTING AND DRYING

Thesis Submitted in Partial Fulfilment
of the Requirements for the Degree of
MASTER OF SCIENCE
by

Alex Rosenthal, B.Sc., B.Ed.

Carried out under the direction of Dr. R.K. Brown.

Time devoted to thesis work was 11 months.

Department of Chemistry
University of Alberta,
Edmonton, Alberta.

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# INTRODUCTION

The work as outlined in this thesis deals with the modification of the properties of cotton linters brought about by alternate wetting and drying cycles. These changes in properties are revealed by accessibility measurements, degree of nitration, viscosity determinations of the nitrates and lead tetraacetate oxidation of the nitrates.

Cellulose, one of the polysaccharides, constitutes the major portion of the skeleton structure of higher plants. Technically speaking, "cellulose" denotes the residues obtained by subjecting vegetable material to certain pulping processes (1). The purest form of raw cellulose is obtained from two types of hair found on the cotton seed, namely, lint and fuzz fibers, more commonly called cotton and cotton linters, respectively. Lint fibers are chiefly used in the textile industry, whereas cotton linters find their greatest use in the preparation of chemical cotton which is subsequently used for the manufacture of such products as nitro-celluloses and rayons.

The now generally accepted concept of the cellulose molecule (Fig. 1) is the result of more than one hundred years of research on the behaviour of cellulose under the most varied treatments. This expresses the chemical behaviour of cellulose. Upon complete hydrolysis only

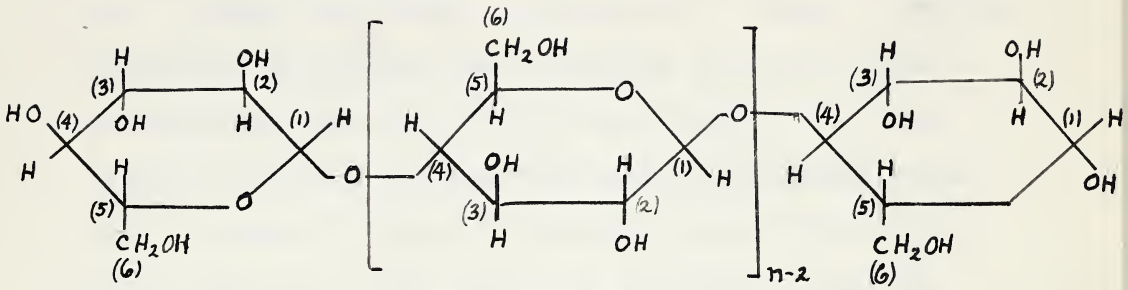
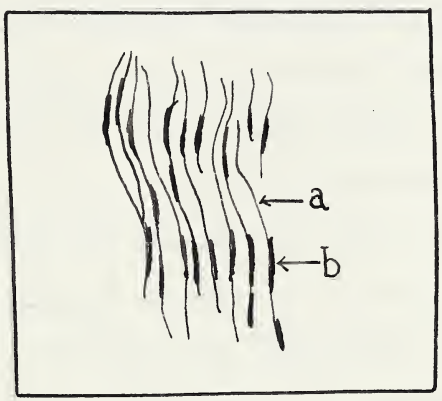


Fig. 1.- Plane projection of cellulose chain of glucose units.




a - amorphous cellulose
b - crystalline cellulose

Fig. 2.- Schematic representation of cellulose structure.

D-glucose is produced. It is believed that the cellulose molecule in the natural state contains several thousand glucose anhydride units linked through the 1 and 4 carbon atoms with a $\beta$-glucosidal linkage. However, it must be understood that cellulose does not consist of identical molecules of the same length. The term "degree of polymerization" represents an average value for the number of glucose anhydride units in the cellulose molecule in any sample of cellulose. Thus the degree of polymerization of cotton lint is 2020, whereas that of cotton linters is 1440 (1). Partially hydrolyzed cellulose may drop into the range 50-500 and still retain the characteristics of cellulose.

Different theories regarding the physical structure of cellulose fibers have been advanced by many workers during the past ninety years. Nageli (2), one of the first of the cellulose chemists, postulated that all cellulose fibers were built up of submicroscopic, anisotropic crystalline particles which he called micelles. Herzog (2), considered the fiber to be a two-phase system, consisting of a crystalline and an inter-crystalline material. Mark (3), in his summary of the theories of cellulose structure, stated that in addition to the crystallized portions, each cellulose filament contains an appreciable amount of amorphous,

or at least badly disordered material (Fig. 2). The tenacity and strength of the cellulose are located in the crystals; the elasticity and extensibility in the amorphous portions.

Nickerson and Habrle (4), by use of a differential hydrolytic method of analyses, found that, in purified cotton fibers, cellulose appeared to exist in three distinguishable states of organization. The three states, amorphous, mesomorphous, and crystalline, are present in amounts of 3%, 3%, and 94%, respectively. The amorphous cellulose is characterized by its highly hygroscopic nature and by a minimum of resistance to hydrolysis. Mesomorphous or transitional cellulose appears to hydrolyze less readily and to be more heterogeneous. Crystalline cellulose exhibits high and uniform resistance to hydrolysis. In hygroscopic and hydrolytic behaviour the mesomorphous component bears a closer resemblance to the crystalline than to the amorphous component.

By means of X-ray analyses, Berkley and Kerr (5) found little or no evidence of crystalline cellulose in the undried cotton fibers taken from the developing bolls. The pattern of native cellulose appeared at the time the fibers underwent their initial dehydration. In the living boll the hydroxyls on adjacent chains are separated by water molecules. The type of hydrogen

bonding associated with crystalline cellulose apparently does not occur until a certain portion of the water is lost (5).

Both chemists and manufacturers of cellulose products have, for many years, known that water affects the physical structure of cellulose. One of the most pronounced visible outward effects is the swelling power of water on either an unpurified or purified cellulose.

There are two types of swelling, namely, intramicellar and inter-micellar (6). In the former type the liquid penetrates the interior of the crystallites or micellae. This type of swelling occurs when cellulose is soaked in aqeous solutions of concentrated caustic soda. In the latter type of swelling the liquid affects the amorphous (or non-crystalline) region only. Prior to the time when heavy water began to be used as an analytical tool for the elucidation of reactions and structure, it was commonly believed that ordinary water was capable of producing only intermicellar swelling, failing to penetrate the crystalline portion of cellulose. Bonhoeffer, as well as Champetier and Viallard, showed that treatment of cellulose with heavy water replaced, by deuterium, three hydrogen atoms in every glucose residue (7). Frilette, Hanle and Mark (8) also observed that heavy water penetrated

the whole mass of cellulose, including the crystallites, and concluded that ordinary water must do so likewise. It is generally agreed that any liquid which causes swelling must be capable of breaking the secondary valence bonds between the cellulose molecules and of forming their bonds with the cellulose. Cellulose swollen with water suffers an increase in volume of the solid but the total volume is less than that of the original solid plus liquid. The change is believed to be due to a compression of the water and cellulose molecules caused by the attraction of the water molecules by hydroxyl groups of the cellulose. Organic liquids, in general, swell cellulosic materials less than water. Kress and Bialkowsky have shown that water has 22 times greater swelling effect than butyl alcohol (9). According to them, the water molecule being smaller than the butyl alcohol molecule, can enter more readily the capillaries of smaller diameter.

The great affinity of dry cellulose for water is attributed to the hydrogen bonding capacity of the hydroxyl groups because a gradually increasing masking of the latter by esterification progressively reduces the amount of moisture absorbed from standard, humid surroundings (10). The sorption of water may be said to take place in three stages (10, 11). The first

avid adsorption is due to the strong hydrogen bonding of single molecules of water to all of the alcoholic groups accessible to water in the amorphous portion of the cellulose. The intermediate adsorption of water corresponds to the filling up of the finer capillaries. In the final adsorption, cellulose swells and there is condensation of free or unbound water in the coarser capillaries.

Purves and co-workers (11) found that a cellulose of known percentage accessible surface, when allowed to adsorb only small amounts of water (6% to 9%) underwent further swelling with a consequent increase in accessible surface, the effect being about 20% increase for materials of high available surface but as much as thirty-fold for those of small degree of disorder. Schur and Hoos (12) found that occasionally cellulose, which had been shredded in the presence of water, subsequently redried, and then nitrated, gave nitrates which had higher nitrogen content than similar cellulose which had been shredded in the dry state and then nitrated. One might be led to believe that the moisture in the cellulose during shredding and subsequent redrying increased the degree of nitration.

Scientists in the field of cellulose industry have realized the importance of selection and control

in the preparation of cellulosic raw materials for the production of a rigorously uniform product. Ball and co-workers (13) have pointed out that carefully standardized tests used in polymer manufacture give good duplicability between various laboratories as long as the test specimens come from the same source, otherwise such measurements are often found to be widely discordant in spite of precautions in standardizing test procedures. An increase in the accessible cellulose can be brought about by the industrial procedure of beating pulps (14). Even the simple action of combing the cotton fibers is said to cause an increase in the amount of "ordered cellulose" (5). Nickerson stated that cellulosic material behaves like an elastic gel. Aqueous swelling, in the case of cotton fibers, coincides with a marked decrease in rigidity and increase in plasticity (15). It is quite obvious, therefore, that the growing conditions affecting the plant, the presence or absence of water in contact with the cellulosic material during its manufacture, and the mechanical manipulation of the raw material, all play an important role in the determination of the physical structure and chemical reactivity of cellulose.

This investigation was undertaken in an attempt to determine more fully the role of water in affecting

the properties of cellulose. In order that swelling effects of water be magnified, the cellulose was alternately wetted, dried, re-wetted, and re-dried, for as many as seventeen cycles (See Tables I-V) pp. 27-33. To determine whether the manner of drying influenced the change of properties of the cellulose, samples of the same batch of cellulose were wetted identically but were dried differently, that is, the samples of one batch of cellulose were dried over phosphorus pentoxide under vacuum, and those of another batch were dried over concentrated sulphuric acid at atmospheric pressure. The methods of drying the samples are discussed in detail in the experimental section.

One of the more powerful swelling agents of cellulose is concentrated aqueous sodium hydroxide. It is believed that the two components, caustic soda and cellulose, combine to form a definite chemical compound having the composition represented by $(C_6H_{10}O_5)_2 \cdot NaOH$ or $C_6H_{10}O_5 \cdot NaOH$, depending upon the concentration of alkali employed. This compound, termed alkali cellulose, is characterized by greater reactivity than the cellulose from which it is obtained, provided that it is not too rigorously dried. This is due principally to swelling action of the alkali solution. Recently Purves and Brown (16) have shown that cellulose swollen by caustic soda of mercerizing strength, dried by

solvent exchange and subsequently collapsed by soaking with water, followed by direct redrying over phosphoric anhydride under vacuum, suffered a decrease in reactivity, as brought out by the fact that the nitrogen content of a technical nitrocellulose prepared from it had been decreased by 0.15 to 0.60%. Jayme (17) had previously found that cellulose dried under different conditions exhibited different reactivities. Samples which had been more intensively dried (that is, which had been dried at higher temperature) suffered a decrease in the ability to reabsorb and retain water. To account for this characteristic Jayme suggested that a state of "hornification" occurred within the cellulosic fibers as a result of the intensive drying. During the intensive drying process, a denser arrangement occurred in the region of the polysaccharide chain through the forces of adhesion and cohesion.

It is obvious that the effects of swelling agents, of mechanical forces, and of unpredictable natural forces, have shown a need of analytical tools which would serve to elucidate fully the fine structure of cellulose. Unfortunately, the methods of measurement of molecular order and disorder in cellulose fibers give results which indicate that they do not always measure the same quality even in a uniform sample of cellulose. The initial, rapid hydrolysis and oxida -

tion of various celluloses has been quantitatively measured by Nickerson, and attributed only to the accessible portion (15, 18). Philipp, Nelson and Züfle, using a method of heterogeneous hydrolysis of cellulose, found that there are two distinct rates which are attributed to the rapid hydrolysis of the loose amorphous regions and to the slow hydrolysis of the loose amorphous regions and to the slow hydrolysis of the dense crystalline portion of the fiber (19). Goldfinger, Siggia, and Mark, using periodic acid as an oxidizing agent, found that the rate of oxidation of cellulose took place in two steps, and this could best be explained by assuming that the sample consisted of more easily and more difficulty accessible areas (20). Of more recent development is the use of heavy water as an analytical tool to measure accessibility (8). This latter method, used by Frilette, Hanle, and Mark, gives an empirical value of total accessibility, whereas the value of crystallinity is only an approximation. The thallation and methylation method of Purves tests the texture of the sample in the bone-dry state and indicates only those domains as accessible that can be penetrated by an organic solvent (14). It has the advantage that the reagents employed produce no swelling of the cellulose during the determination.

The thallation method of Purves (14) was used in our research in the estimation of the accessibility of swollen samples. In this procedure thallous ethylate, produced as represented by the equation below, is used as the thallating agent:

$$2Tl + 2\ EtOH \longrightarrow TlOEt + H_2$$

The thallous ethylate reacts with the cellulose producing thallous cellulosate:

$$TlOEt + \text{cellulose } OH \longrightarrow \text{cellulose } OTl + EtOH$$

This reaction is restricted to those hydroxyls which are accessible to the thallous ethylate in ether solution. Methyl iodide, used as the methylating agent, replaces the thallium. The methoxyl substitution of the partly methylated cellulose is accepted as proportional to the number of hydroxyl groups that have come in contact with the thallous ethylate reagent. The reaction is represented as follows:

$$\text{cellulose } OTl + CH_3I \longrightarrow \text{cellulose } OCH_3 + TlI$$

The methoxyl content of the methylated cellulose was determined by the method of Hoffmann and Wolfrom (22), which is a modification of the volumetric procedure of Viebock and Schwappach (23). The methyl of the $CH_3O$ group is converted into methyl iodide (Zeisel's method) by boiling with hydriodic acid, and the methyl iodide is converted into the corresponding bromide with formation of iodine bromide:

$$\text{cellulose } OCH_3 + HI \longrightarrow CH_3I + \text{cellulose}$$

$$CH_3I + Br_2 \longrightarrow CH_3Br + BrI$$

The iodine bromide is ozidized to iodic acid by excess of bromine:

$$BrI + 2\,Br_2 + 3H_2O \longrightarrow HIO_3 + 5HBr$$

The excess of bromine is converted into hydrobromic acid by means of formic acid and finally, after the addition of potassium iodide, the iodine liberated is titrated with sodium thiosulphate:

$$HIO_3 + 5KI + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

$$2Na_2S_2O_3 + I_2 \longrightarrow S_4O_6^{=} + 2I^- + 4Na^+$$

Since in this method, six equivalents of iodine are liberated for each methoxyl group, the determination of total methoxyl content can be made with great accuracy even when the amounts of substance are very small.

Changes in the reactivity of cellulose, caused by pretreatment of the cellulose with swelling agents, reveal themselves in the properties of the derivatives of cellulose (16, 24). Nitrocellulose is one of the most important of the cellulose derivatives, finding its chief use as a propellant during war. It is known that nitrocelluloses, manufactured under identical conditions, perform differently when tested as propellants. The cause of this erratic behaviour is of vital concern to those responsible for its manufacture and subsequent use (25).

Cellulose may be nitrated in a number of differ-

ent ways. Nitric acid-sulphuric acid mixtures give nitrates with nitrogen content up to 13.7% (26). Nitrocelluloses with a nitrogen content close to the theoretical 14,17% (trinitrate), can be produced with a nitric acid- phosphoric anhydride mixture (27). Mixtures of glacial acetic acid, acetic anhydride, and nitric acid have also been used as nitrating agents (28). Wannow used a nitric acid/phosphoric acid mixture for the preparation of nitrocellulose.

Although cellulose can be nitrated with concentrated nitric acid alone, nitration is, in practice, always effected by the use of a mixture of nitric acid-sulphuric acid. The nitrogen content of the products obtained depends upon the amount of water present in the reaction mixture. Technical nitration mixtures can be made up according to the table assembled by Dorée (26) to yield nitrated celluloses of 6.50 to 13.65 per cent nitrogen. The nitrogen content of the mono , di , and trinitrate are 6.77%, 11.13%, and 14.17% respectively. The highest nitrogen is obtained with a system represented by $HNO_3 + n(H_2SO_4.H_2O)$, and the lowest when the nitric acid is present as the hydrate $HNO_3.H_2O$ (26). The sulphuric acid appears, therefore, to act by dehydrating the nitric acid.

The rate of nitration of cellulose increases with rise in temperature, but degradation of the cellulose molecule also increases. Berl has pointed out that

this degradation can be reduced with a nitric acid-phosphoric anhydride mixture (27). Schur and Hoos (12) stated that esterification, oxidation, and hydrolysis may take place to a greater or lesser extent, according to the composition of the nitrating mixture, the ratio of liquid to the cellulose, the temperature, the intensity of agitation, and the physical condition of the cellulose. As nitration proceeds, water and heat are generated, and nitric acid is consumed. If the reaction proceeds too rapidly, the acid immediately adjacent to the fiber, or within it, may grow so rich in water and so poor in nitric acid that hydrolysis is promoted. In addition, localized generation of heat may lead to oxidation and to hydrolysis of the cellulose.

In the industrial field, the mechanical dipping process and the displacement process (29) are commonly used in the production of cellulose nitrates from cellulose and nitric acid-sulphuric mixtures. In the former method the cellulose is immersed in the nitrating mixture and kept there for thirty minutes under continual agitation, whereupon the acid is removed by centrifugal force. The nitrate, after being drowned in sufficient water, is washed and stabilized. In the displacement process, pans with perforated false bottoms are filled with mixed acid; then cotton is added and covered with a perforated plate so that the cotton

is completely submerged. At the end of nitration, the spent acid is drained off slowly and is displaced at the same time with water. These two methods can be adjusted to yield nitrocelluloses of identical nitrogen content but with different general properties. Since this difference is not accidental, it points to the necessity of carefully standardizing all conditions of nitration of the cellulose.

In a laboratory, uniform products are obtained by nitrating small batches of cellulose (approximately one gram in each batch), by carefully controlling weight of cellulose and acid mixture, by keeping the nitration time and temperature constant, and by shaking the flask. The crude nitrate is contaminated with nitrating acid, sulphuric acid esters of the cellulose, and nitro compounds produced from the impurities in the fiber employed. These impurities, which would render the product liable to spontaneous decomposition, are removed by washing, and then boiling the cellulose nitrate in a water-ethanol solution (a process known as stabilization).

Determinations of the viscosity of cellulose nitrate in butyl acetate may be used as a tool to help ascertain effects of a reagent, such as water, on cellulose. Staudinger found that the viscosity of a dilute solution, in a neutral solvent, of a long-chain polymer

is a function of the number of groups, or "submolecules", contained in the chain. The glucose anhydride residue, of weight 162, is the submolecule of cellulose. If $\eta$ is the viscosity of a solution of concentration "C", where "C" is the per cent concentration by weight of the solution, and $\eta_o$ is the viscosity of the pure liquid solvent, then the quantity, $\eta_{sp}$, which is equal to $\eta/\eta_o - 1$ is used to represent the specific viscosity of the solution. The value of $\eta_{sp}/C\%$, which does not vary greatly with concentration, at low concentrations is approximately a linear function of the latter variable, and extrapolation to zero concentration gives the intrinsic viscosity of the solution $[\eta]$. In the work carried out $\eta_{sp}/C\%$ was determined after each successive dilution of a given solution (See Experimental Section) and the value of $\eta_{sp}/C\%$ was taken to be equal to $[\eta]$ when it no longer changed in value upon further dilution of the given solution. As the viscosimeter, the volume of solution, the solvent, and temperature, were the same in all determinations, then the relative viscosities in dilute solutions were taken as proportional to the time of flow.

The Intrinsic Viscosities, obtained as directed in the preceding paragraph, were taken to be proportional to the degree of polymerization (30). They are, however, easily converted to numerical values repre -

senting the degree of polymerization by resorting to the Staudinger equation,

$$\lim_{C \to 0} \left[ \frac{\eta_{sp}}{C_{submoles}} \right] = K_m M$$

where

$C_{submoles}$ = Concentration in submoles per liter.

$K_m$ = A constant.

M = Molecular weight of the macromolecule.

Since the Concentration in submoles, expressed as a per cent = $\frac{\text{Weight of a submole}}{1000} \times 100\%$,

therefore, $\frac{\text{Concentration}\%}{\frac{\text{Submolar weight}}{1000} \times 100} = \text{Concentration in submoles,}$

where Concentration % = Concentration in grams per 100 ml.

Therefore the Staudinger equation can be written as:

$$\lim_{C \to 0} \left[ \frac{\eta_{sp}}{C_{submoles}} \right] = \lim_{C \to 0} \left[ \frac{\eta_{sp}}{C\%/\frac{\text{submolar wt.} \times 100}{1000}} \right] = K_m M$$

or $$\lim_{C \to 0} \left[ \frac{\eta_{sp}}{C\%} \right] = \frac{K_m M}{\text{Submolar wt.}} \times 10$$

But the Molecular Weight (M) = D.P x Submolar weight, where D.P. is the Degree of Polymerization.

Therefore, $$\lim_{C \to 0} \left[ \frac{\eta_{sp}}{C\%} \right] = 10 K_m \text{ D.P.} = [\eta]$$

According to the work of Kraemer (31), evaluation of constant, $K_m$, gives the relation:

$$\text{D.P.} = 270[\eta]$$

Coppick and Jahn (32) have suggested that severed linkages between the glucose anhydride units of the

cellulose molecule result in a decrease in viscosity. The cooking processes used for isolating cellulose are more effective than nitration in reducing the chain length of the cellulose. Aging, relatively high temperatures, and light (29) cause a lowering of viscosity of solutions of cellulose nitrates. Kraemer found that pure acetone solutions of cellulose nitrate show the greatest decrease in viscosity after eight days (29,31). High temperatures of drying (105°) lead to thermal degradation and lowering of viscosity of solutions of cellulose nitrate (33). Nitrocellulose viscosity may be influenced by the viscosity of the original cellulose and the conditions of nitration. An increase in nitration time and temperature lead to a lowering of viscosity of the resulting nitrate solutions (34). Wannow found that viscosity of nitrocellulose increased with increase in degree of substitution, provided that the degree of polymerization remained constant (35).

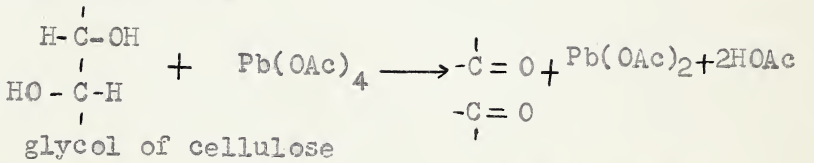
Without doubt, a knowledge of the position and extent of substitution in a nitrocellulose would help to reveal changes in reactivity of cellulose caused by swelling agents. On examination of Figure 1 (page 2), it can be seen that there are two kinds of hydroxyls, namely primary and secondary. The former is located on carbon six, and the latter exists as a trans glycol group on carbons two and three. The primary hydroxyl,

on partially acylated celluloses, has been determined with varying degrees of success by use of the tosylation and iodination method (26, 37, 38, 39). An attempt has been made to determine which hydroxyls are unesterified in nitrated celluloses (40). An analytical tool which would disclose whether the substitution of hydroxyls by nitro groups had been ordered or random would help reveal the mechanism of the nitration reaction. Since the primary hydroxyls are more sterically exposed, it might be assumed that they would be nitrated first. Thus by making a mononitrate of cellulose, one might again assume that the trans glycol group on carbon two and three would still be available for oxidation. Lead tetraacetate, which preferentially cleaves unesterified glycol groups, is used to determine what fraction of the total hydroxyls exists as glycol groups.

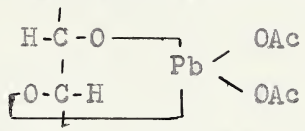
Hockett, Cramer, and Purves oxidized commercial acetone-soluble cellulose acetates with lead tetraacetate and found that the distribution of hydroxyls on a partially acylated cellulose was largely a matter of chance (41). Purves and Brown (42) oxidized commercial cellulose nitrates to small but variable extents. They found that wetting and redrying of highly swollen linters prior to technical nitration increased the level of oxidation. As a result of this evidence, oxidation of cellulose nitrates of varying

nitrogen content was undertaken in an attempt to gain some information concerning the manner of substitution in the glucose anhydride unit of cellulose.

An investigation of the mechanism of glycol cleavage by lead tetraacetate has been presented by Heidt, Gladding and Purves (43). The hydroxyl groups of the glycol in the cellulose must be in a free unesterified condition.




Lead tetraacetate condenses with glycols to form an unstable cyclic ester with Pb as its central atom. The valence of the central atom is immediately reduced by two units resulting in the production of acetic acid and lead acetate. Thus one mole of lead tetra-




acetate would be required to split one glycol group in one glucose anhydride unit. By plotting consumption of oxidant against time, one could determine when the oxidation of the nitrocellulose is complete by noting the point at which the curve will have zero slope. The height of the ordinate, at zero slope of the curve, would therefore represent the total consumption of the oxidant by the cellulose nitrate. From this data it

should be relatively simple to determine whether the nitration occurred in an ordered or random way. Moreover, decided breaks in the oxidation rate curve might indicate different domains of the cellulose nitrate which are more or less accessible to oxidation.

# EXPERIMENTAL

## A. PREPARATION OF CELLULOSE SAMPLES

A quantity of high grade cotton linters, the gift of H. M. Spurlin and the Hercules Powder Co., was dewaxed by extraction in a Sohxlet apparatus for two days with a mixture of ethanol and benzene (1:2). The purified product was dried in air and subsequently stored in a closed container.

### 1. Swelling of Cellulose Samples with 10% Aqueous Sodium Hydroxide

The samples of cellulose were swollen using the modification of the swelling technique discovered by Glegg's modification (44) of the procedure developed by Assaf, Haas and Purves (21). Fifteen g. of dewaxed, airdried cellulose were immersed in 540 ml. of 10% sodium hydroxide solution at 5°, and two and a half hours later the swollen mass, together with the caustic, were poured into an amount of 10% aqueous acetic acid (also previously cooled to 5°) calculated to neutralize the caustic soda used in the swelling process. After a period of 10 minutes, during which the mixture was stirred at intervals to permit complete diffusion of the acid through the cellulose, the aqueous portion was decanted and the solid pressed free from excess liquid. A second treatment with 1 ½

liters of 1% acetic acid for 10 minutes rendered the solution slightly acidic and removed the last traces of sodium hydroxide. This solution was decanted as before, and replaced by 1½ liters of distilled water, which was thoroughly mixed with the cotton for three or four minutes and then drained away. About six separate washings with 1½ liter volumes of distilled water were necessary to free the cellulose from salts and acid (litmus test). The excess water was squeezed from the linters by gentle pressure and the wet mass quickly dispersed, and occasionally stirred, in one liter of 99% methanol. Fifteen minutes later, the methanol was removed and replaced by a fresh amount, and this process was continued for three additional washings. Two more immersions for 30 minutes each, in magnesium dried methanol (45), were followed by four more, one of 30 and three of 15 minutes each, in one-liter volumes of sodium-dried, thiophenefree benzene, to remove the last traces of methanol. The supernatant liquids were easily reclaimed and purified. During all the manipulations, care was taken to avoid even superficial drying of the cellulose, since such drying tended to give a non-uniform product.

The swollen linters, wet with benzene, were dried in a desiccator over containers of phosphoric anhydride and paraffin for several days, during which frequent changes of the drying reagent, and repeated evacuation

of the desiccator to a pressure of about 25 mm. mercury were necessary in order to produce a material free from the odour of benzene. The product was then stored in the usual manner (21) in a desiccator for one week over concentrated sulphuric acid.

2. Cellulose Sample Swollen with Distilled Water and Dried by Solvent Exchange

A sample of cellulose, soaked in distilled water for four hours, was then taken out, and squeezed gently to remove excess water. The sample was dried by solvent exchange as stated previously in 1.

3. Collapse of the Dried Swollen Linters to an Accessibility of 0.2-0.4%

Half of the dried linters was soaked in water for twenty minutes, squeezed gently to remove excess liquid, and then dried directly under vaccum over phosphoric anhydride. When thoroughly dry, the linters were stored, along with the dried swollen portion, over concentrated sulphuric acid in the same desiccator.

4. Swelling of Cotton Linters with Distilled Water by a Cyclical Process

(a) Drying over Phosphoric Anhydride Under Vacuum

A quantity of air-dried cellulose was immersed in distilled water for a period of twelve hours, the water then decanted and the swollen mass gently pressed by hand to remove excess water. The cellulose was then reduced to dryness over phosphoric anhydride under vacuum. A two-gram sample of the dried product was retained and the remainder again treated with a large excess of water for three hours and then dried as before. This procedure of three-hour immersion followed by intensive drying was repeated in order to obtain a series of dried samples of cotton linters differing only in the number of times they had been soaked with water and dried. (This series is indicated in Table I.)

TABLE I

WETTING CYCLE OF COTTON LINTERS IN DISTILLED WATER

Samples Dried over Phosphoric Anhydride under Vacuum and Stored in the Dark, at Room Temperature, over Concentrated Sulphuric Acid

| Sample | Length of Wetting in hours |
|---|---|
| V-1 | 12 |
| V-2 | 3 |
| V_3 | 3 |
| V-4 | 3 |
| V-5 | 3 |
| V-6 | 3 |
| V-7 | 3 |
| V-8 | 3 |
| V-9 | 3 |

Another series of samples of cellulose, swollen in identical manner to that above, was first partially dried in air at room temperature, and subsequently dried over phosphoric anhydride under vacuum. (See Table II.)

TABLE II

WETTING CYCLE OF COTTON LINTERS IN DISTILLED WATER

Samples Dried in Air, then over Phosphoric Anhydride under Vacuum, and Stored in the Dark, at room Temperature over Concentrated Sulphuric Acid

| Sample | Length of wetting in hours | Time of drying in air in days | Time of drying over $P_2O_5$ under vacuum in days | Weight of sample retained in g. |
|---|---|---|---|---|
| X-1 | 12 | 3 | 2 | 3 |
| X-2 | 3 | 1 | 1 | 0 |
| X-3 | 3 | 1 | 1 | 3 |
| X-4 | 3 | 1/2 | 1 1/2 | 0 |
| X-5 | 3 | 1/2 | 2 1/2 | 3 |
| X-6 | 3 | 1/2 | 1 1/2 | 0 |
| X-7 | 3 | 1/2 | 2 1/2 | 3 |
| X-8 | 3 | 1 | 3 | 0 |
| X-9 | 4 | 1 | 2 | 3 |
| X-10 | 3 | 1 | 14 | 0 |
| X-11 | 3 | 1 | 2 | 0 |
| X-12 | 3 | 1 | 4 | 0 |
| X-13 | 3 | 1 | 4 | 0 |
| X-14 | 3 | 1 | 4 | 0 |
| X-15 | 3 | 2 | 3 | 3 |

(b) Samples Dried in Air and Stored over Sulphuric Acid

Concurrently, a third quantity of the dewaxed linters was given identical treatment to that above with the only difference that the cellulose was merely air-dried at room temperature after each soaking with water. (Tables III and IV.) The samples were stored over concentrated sulphuric acid at room temperature.

TABLE III

WETTING CYCLE OF COTTON LINTERS IN DISTILLED WATER

Samples Dried in Air and Stored in the Dark, at Room Temperature over Concentrated Sulphuric Acid

| Sample | Length of wetting in hours | Time of drying in air in days | Weight of sample retained in g. |
|---|---|---|---|
| Y-1 | 12 | 5 | 3 |
| Y-2 | 3 | 2 | 0 |
| Y-3 | 3 | 2 | 3 |
| Y-4 | 3 | 2 | 0 |
| Y-5 | 3 | 3 | 3 |
| Y-6 | 3 | 2 | 0 |
| Y-7 | 3 | 3 | 3 |
| Y-8 | 3 | 4 | 0 |
| Y-9 | 3 | 3 | 3 |
| Y-10 | 3 | 2 | 0 |
| Y-11 | 3 | 3 | 0 |
| Y-12 | 3 | 2 | 3 |
| Y-13 | 3 | 2 | 3 |
| Y-14 | 3 | 2 | 3 |
| Y-15 | 3 | 2 | 3 |
| Y-16 | 3 | 2 | 3 |
| Y-17 | 3 | 2 | 3 |

All the samples of cellulose indicated in Tables I-IV were stored in the dark, at room temperature, for

at least one week in a large desiccator over concentrated sulphuric acid at atmospheric pressure.

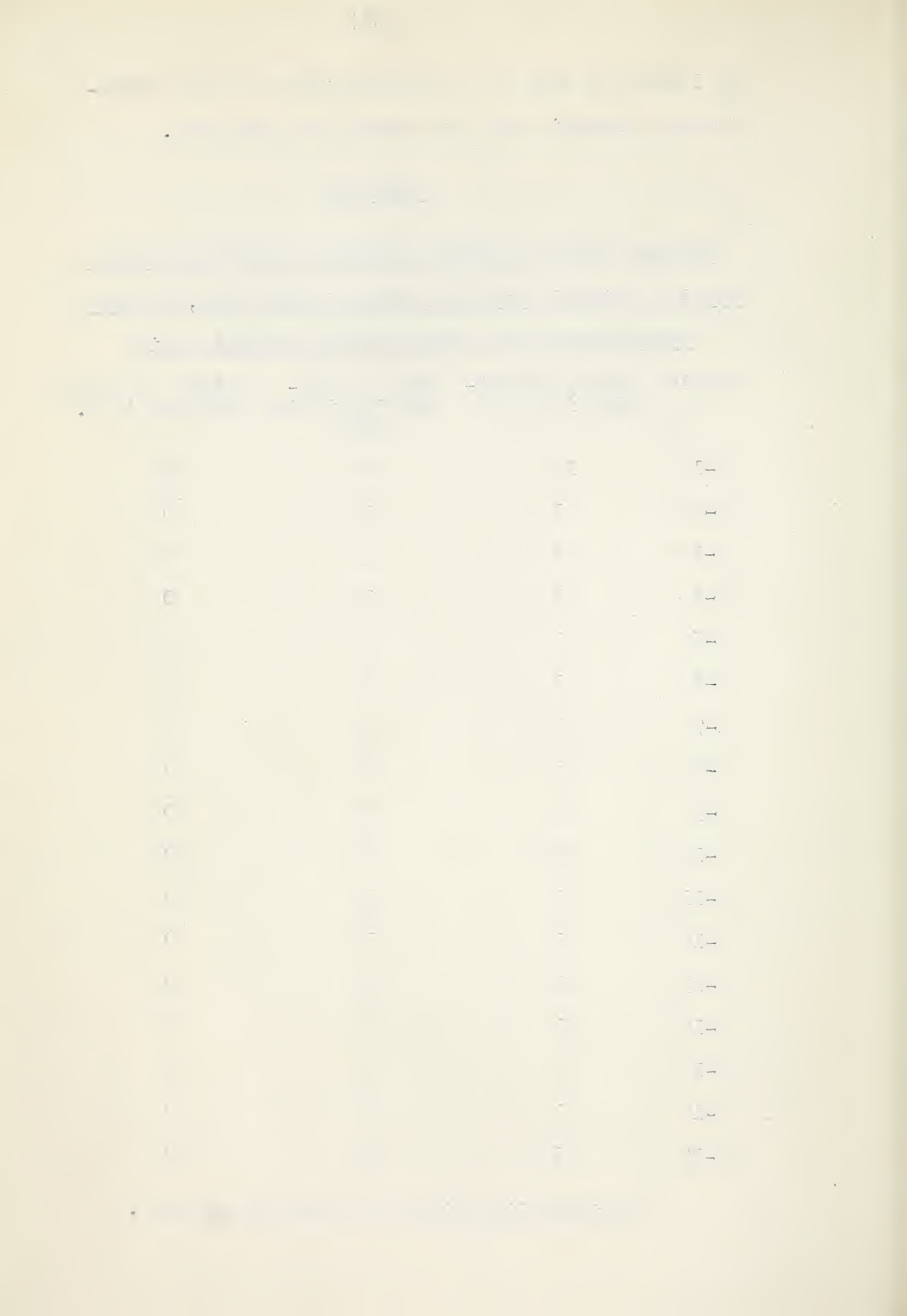
TABLE IV

WETTING CYCLE OF COTTON LINTERS IN DISTILLED WATER

Samples Dried in Air and Stored in the Dark, at Room Temperature over Concentrated Sulphuric Acid

| Sample | Length of wetting in hours | Time of drying in air in days | Weight of sample retained in g. |
|---|---|---|---|
| R-1 | 10 | 2 | 20 |
| R-2 | 3 | 3 | 0 |
| R-3 | 3 | 2 | 0 |
| R-4 | 3 | 3 | 0 |
| R-5 | 3 | 2 | 20 |
| R-6 | 3 | 2 | 0 |
| R-7 | 3 | 2 | 0 |
| R-8 | 3 | 2 | 0 |
| R-9 | 3 | 3 | 0 |
| R-10 | 9* | 2 | 20 |
| R-11 | 3 | 3 | 0 |
| R-12 | 3 | 3 | 0 |
| R-13 | 3 | 2 | 0 |
| R-14 | 3 | 2 | 0 |
| R-15 | 3 | 2 | 0 |
| R-16 | 3 | 2 | 0 |
| R-17 | 3 | 2 | 20 |

* Incidentally allowed to soak for 9 hours.



(c) Samples Dried in Air and Stored in a Closed Container Without any Drying Agent

A fourth quantity of the dewaxed linters was given identical treatment to that of 4 (b) page 28, with the only difference that the cellulose was stored at room temperature in a closed container without any drying agent present. (Table V)

TABLE V

WETTING CYCLE OF COTTON LINTERS IN DISTILLED WATER

Samples Dried in Air and Stored in the Dark, at Room Temperature, in a Closed Container with no Drying Agent

| Sample | Length of wetting in hours | Time of drying in air in days | Weight of sample retained in g. |
|---|---|---|---|
| Z-1 | 12 | 2 | 3 |
| Z-2 | 3 | 2 | 0 |
| Z-3 | 3 | 2 | 3 |
| Z-4 | 3 | 3 | 0 |
| Z-5 | 4 | 2 | 2 |
| Z-6 | 3 | 14 | 0 |
| Z-7 | 3 | 1 | 0 |
| Z-8 | 3 | 1 | 0 |
| Z-9 | 3 | 2 | 3 |
| Z-10 | 7 | 2 | 0 |
| Z-11 | 3 | 2 | 0 |
| Z-12 | 3 | 2 | 1 1/2 |
| Z-13 | 3 | 2 | 0 |
| Z-14 | 3 | 2 | 2 |
| Z-15 | 3 | 2 | 0 |
| Z-16 | 3 | 3 | 2 |

5. Prolonged Soaking of Cotton Linters in Distilled Water

Concurrently with the wetting cycles carried on

as indicated in A-4, pp. 25-33, another small quantity of air-dried dewaxed cotton linters was immersed in distilled water for twenty days, (a time equivalent to that required for seven cycles of wetting and drying as shown in Table II), the excess water was then removed and the mass reduced to dryness over phosphoric anhydride under vacuum. Half of this dried cellulose was again immersed in distilled water for thirty days (a time equivalent to that required for the remaining cycles of wetting and drying as indicated in Table II), and then dried as before.

Concurrently, a second quantity of the dewaxed linters was given identical treatment to that above with the only difference that the cellulose was merely air-dried after each soaking with water.

These four samples of cellulose were stored at room temperature in a desiccator over concentrated sulphuric acid.

6. Samples of Swollen Cellulose Subjected to Atmospheric Conditions

Samples of cellulose, prepared as stated in A-4 (b), page 25, were placed in a covered box with perforated sides. The container protected the samples from dust, and yet allowed some movement of air over the cellulose. This box was stored in an unheated

open shed for three months during the winter. A similar set of samples was stored in like manner in a heated basement room in the University of Alberta for six months. (The time difference in storing was due to the fact that the first set of samples which had been exposed to the outside atmosphere was unfortunately destroyed by fire.)

## B. DETERMINATION OF ACCESSIBILITY OF SWOLLEN COTTON LINTERS

### 1. Thallation and Methylation of Dry Cotton Linters

The dry, swollen cotton linters were thallated and methylated using the procedure developed by Purves (21).

The cotton samples, 0.1 to 0.3 g., were transferred from a desiccator into the tared cups and quickly weighed on a balance prior to insertion into the apparatus (Figure 3, p. 36 ). The stopper was replaced promptly to prevent access of moisture and the apparatus was at once evacuated with an oil pump attached to (3). Low results are obtained if this evacuation is neglected. Stopcock (3) was then closed and (1) was opened to permit 0.1 N thallous ethylate solution to be sucked into the apparatus from the separatory funnel. About 20 ml. of solution was sufficient to fill all three cups and immerse them completely. After standing in the

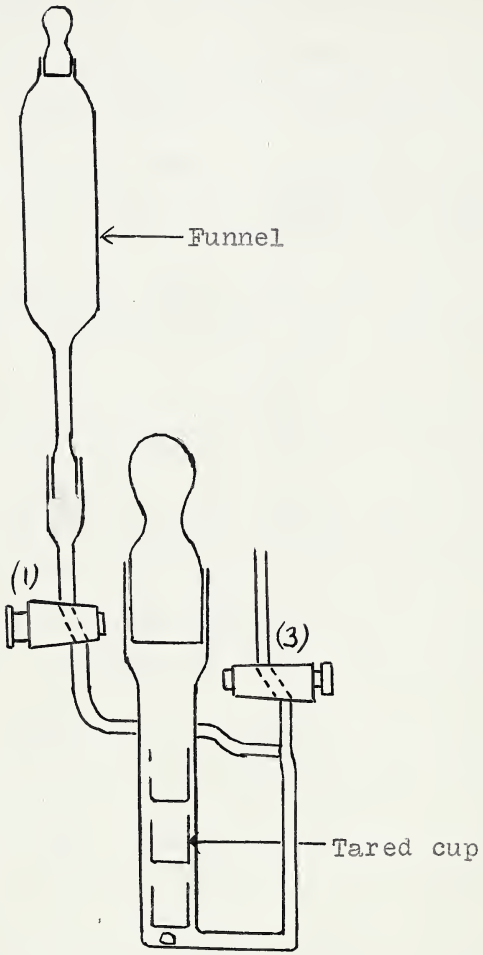



Fig. 3.- Apparatus for thallation and methylation.

dark at room temperature for one hour, the partly exhausted solution was removed by suction through stopcock (3), with a minimum use of a water pump, and the thallation was repeated with fresh solution drawn in through (1). Samples thallated in ether solution were coloured yellow, and, the depth of colour was a rough measure of the extent of thallation. The thallous ethylate solution was withdrawn at the end of the second hour in the dark and residual amounts were washed from the samples by filling the apparatus with pure, dry benzene. Four or five benzene extractions (carried out in the dark), the first of fifteen and the others each of five minutes duration, were sufficient. The wet samples were then prepared for methylation by filling the apparatus with benzene containing a large excess, 2 ml., of methyl iodide. The ground-glass stopper was replaced with a glass-jointed reflux condenser whose upper end was equipped with a calcium chloride tube, stopcocks (1) and (3) were closed and the entire apparatus was immersed up to the level of the upper sample cup in a water-bath kept at 80°. No exclusion of light was necessary during the methylation, which was complete within three and one-half hours. Since thallous iodide was a by-product of the reaction, the methylation was attended by a color change in the samples from

yellow to orange, the intensity of which was a rough measure of the amorphous cellulose. The condenser was then exchanged for the glass stopper and the excess methyl iodide-benzene mixture in the cellulose was removed by suction. The first two benzene extractions, each of fifteen minutes' duration, were followed by six more, each lasting for five to ten minutes. Thoroughness was essential in this extraction lest traces of residual methyl iodide invalidate the final methoxyl estimation. The apparatus was then connected to a water pump, in order to remove the benzene, care being exercised in the beginning, to keep stopcock (3) open only momentarily in order to avoid scattering of the samples by a too sudden evaporation of the residual benzene. After a final drying in high vacuum at 80° for two hours, the the whole of each sample, with its occluded thallous iodide, was analyzed for its methoxyl content. The methoxyl content was expressed as a percentage of the original, unsubstituted cellulose, and multiplied by the factor 100/57.4 gave the percentage of the cellulose hydroxyl groups that had been methylated. This value was assumed to be equal to the percentage of the cellulose wetted by the solvent for the thallous ethylate.

Preparation of Thallous Ethylate Solutions (21)

Thin slices of clean, silvery thallium metal, 2 g., contained in a 125 ml. glass stoppered, thick walled Erlenmeyer flask, were covered with 50 ml. of absolute ethanol, and a stream of dry oxygen gas was played over the surface of the liquid for one to two minutes. The flask was then stoppered, shielded from light, and shaken mechanically. Solution of the metal was complete within two hours if the oxygen at the atmosphere was renewed at 15 minute intervals.

A small piece of porous porcelain was added to the solution to promote uniform boiling during the removal of ethanol under vacuum (water pump). The latter part of the distillation, under vacuum, was from a water bath kept at 30° (thallous ethylate decomposes readily at higher temperature). An excessive use of the pump was avoided lest moisture reach the ethylate when the vapor pressure of the residual alcohol became low. (Protection against moisture was provided by connecting a calcium chloride tube between the Erlenmeyer flask and the water pump). When the flask was shielded from light and the technique of distillation was satisfactory, the residual thallous ethylate formed about 1 ml. of a heavy pale yellow oil. The oil was kept at room temperature for ten minutes under high vacuum to

remove any traces of ethanol and dissolved in 50 ml. of the pure, anhydrous ether. Glass-stoppered graduates of 100 ml. capacity were convenient receptacles for these solutions.

The normality of the thallous ethylate was determined by pipetting 5 ml. in a mixture of 20 ml. of methanol and 10 ml. of 0.1 N hydrochloric acid, the excess of which was then titrated with standard caustic soda. Dilution of the thallous ethylate solution to 0.1 N was made with the appropriate volume of the pure solvent. These solutions did not change their normality during several weeks if kept near $0^{\circ}$ in the dark, but exposure to light caused rather rapid formation of a spongy, brown decomposition. Thallous ethylate oil was also fairly stable when properly stored.

## 2. A Determination of Accessibility by Methoxyl Estimation

The method of Hoffmann and Wolfrom (22), which is a modification of the volumetric procedure of Viebock and Schwappach (23), was used for the determination of the methoxyl content of the methylated cellulose.

At the beginning of a series of determinations the all-glass apparatus (for methoxyl analysis) was

assembled (Fig. 4, p. 42 ), (all ground-glass joints were lubricated with high-vacuum grease) and flushed with a slow stream of carbon dioxide for ten minutes. The gas stream was continued while 8 ml. of constant boiling hydriodic acid (sufficient for two successive determinations) and a one inch piece of nichrome wire (to prevent bumping) were placed in the reaction flask and the scrubber was charged by the upper stopcock (1). The hydriodic acid was then heated, by means of a small flame, to reflux temperature and carbon dioxide passed through the apparatus for an additional twenty minutes to remove last traces of interfering impurities, after which the flames were extinguished, and the reaction flask immediately loosened from the condenser (to prevent sticking of the ground-glass joints).

When the hydriodic acid in the reaction flask had reached room temperature, the flow of carbon dioxide was stopped. The receiver was then rinsed with glacial acetic acid and charged with 10 ml. of the receiver solution ( pp. 44,45 ). After the receiver assembly was set in place, the cellulose sample was quickly placed in the reaction flask, and the latter was then connected to the condenser. The hydriodic acid was then heated to boiling and refluxed gently while just enough carbon dioxide was turned on to prevent the hydriodic acid from back-

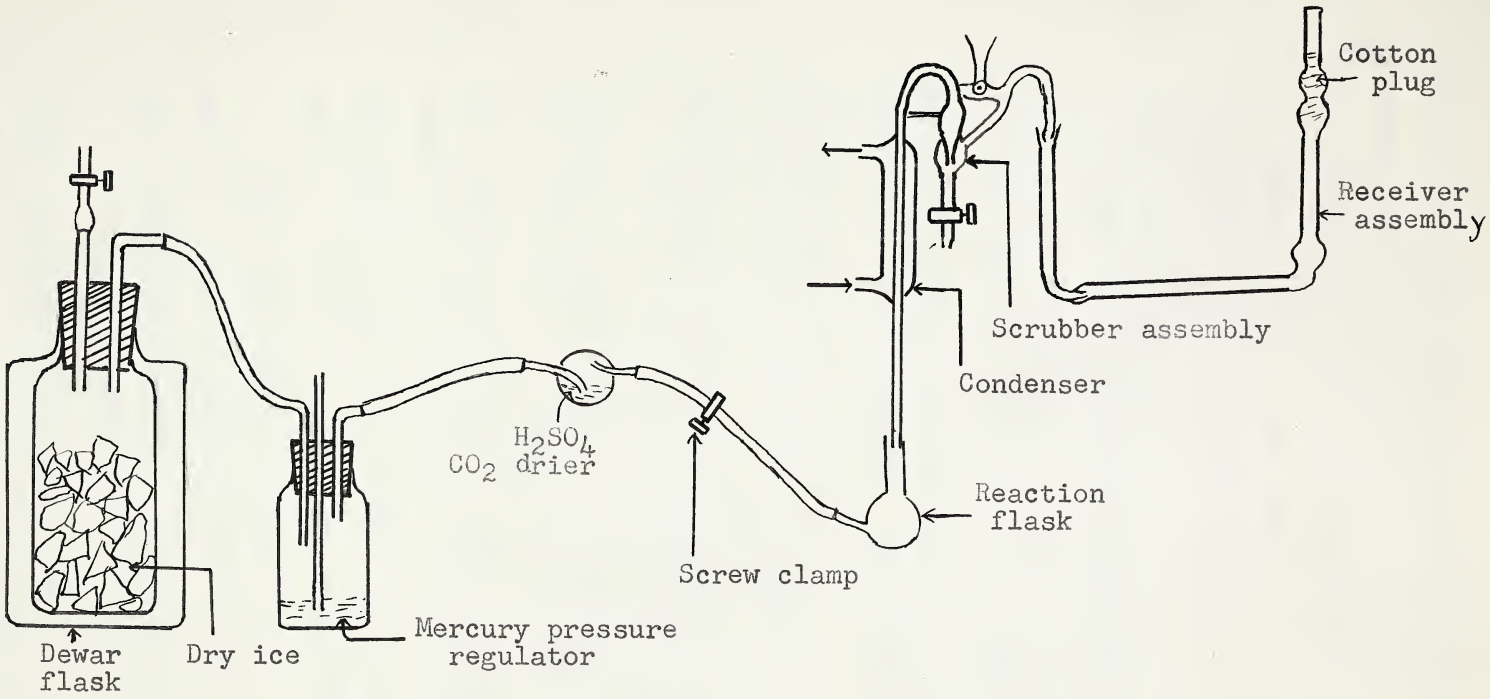



Fig. 4.- Apparatus for methoxyl determination.

ing up into the carbon dioxide inlet tube. The carbon dioxide was adjusted to a rate of 20 to 25 ml. per minute. In initiating the gas flow, care was taken to turn on the carbon dioxide very slowly in order to prevent bumping due to superheating of the hydriodic acid.

As the carbon dioxide passed through the apparatus, the receiver orifice emitted a steady stream of small bubbles, whose time of contact with the receiver solution depended upon the angle at which the receiver was inclined. The entire apparatus was adjusted until the optimum rate of gas flow (20 to 25 ml. per minute) allowed the bubbles to remain in contact with the receiver solution from 5 to 7 seconds.

After at least 30 minutes' sweeping, the receiver was disconnected, the reaction flask was cooled and immediately loosened, the stream of carbon dioxide was stopped, the alternate receiver was filled and assembled, the new sample of methylated cellulose was quickly inserted in the reaction flask, and the procedure described above was repeated.

While the second analysis was in progress, the receiver solution from the first was washed into a 250 ml. Erlenmeyer flask containing 25 ml. of water and 5 ml. of 25% sodium acetate. Ten drops of 90% formic acid were then added, and the flask swirled until the bromine color was discharged. The flask

was then stoppered and shaken by hand in an oscillatory motion, until further shaking failed to develop back pressure inside the flask. An amount of 5 ml. of 10% sulphuric acid was then added, followed by about 0.5 g. (an excess) of potassium iodide. The liberated iodine was titrated with 0.02 N sodium thio-sulphate, using starch as an indicator. The titration was made with a 10 ml. precision buret. The volume of sodium thiosulphate required for a blank determination was subtracted from the volume required for the titration of a known sample.

$$\text{Weight of methoxyl} = \frac{\text{Vol. (in ml.) of } Na_2S_2O_3 \times \text{Norm. of } Na_2S_2O_3 \times 31}{1000}$$

$$\% \text{ Accessibility} = \frac{\text{Wt. of methoxyl}}{\text{Wt. of sample}} \times 100 \times \frac{100}{57.4}$$

Trimethyl cellulose has a methoxyl content of (3x31x100)/162 or 57.4% on this basis.

Reagents for Methoxyl Estimation

The scrubber solution consisted of a mixture of equal volumes of 5% aqueous cadmium sulphate and 5% aqueous sodium thiosulphate.

Carbon dioxide was obtained from dry ice kept in a thermos bottle. The carbon dioxide was dried by passing it through concentrated sulphuric acid, and the gas flow was regulated by means of clamps placed on the rubber tubing (Fig. 4).

The receiver solution was prepared by dissolving

35 g. of potassium acetate in 350 ml. of glacial acetic acid and adding 7 ml. of bromine. The solution was then exposed to daylight (to stabilize the solution) in a clear glass bottle for one week before use. The sodium thiosulphate contained 0.20% of sodium carbonate as a preservative.

## C. Nitrations of Cotton Linters

### 1. Nitrations with Sulphuric Acid - Nitric Acid Mixtures

The nitration procedure was identical to that employed by Brown and Purves (46). Technical nitration mixtures were made up according to the tables assembled by Dorée (26), to yield a nitrated cellulose of about 11.50 per cent nitrogen. Each batch of nitration mixture was checked by sample nitrations of dewaxed, unswollen cellulose, as well as by analysis of the mixture, and suitable corrections in composition were made, if necessary, to give the desired nitrogen content in the nitrocellulose. The actual nitrations were carried out under carefully controlled conditions to ensure duplication of results. One hundred g. of the technical nitration solution was put into a dried, glass-stoppered Erlenmeyer flask of about 200 ml. capacity, and then, after the flask

and contents had been brought to 15°, one gram of the dried cellulose was quickly weighed (to the second decimal place), roughly shredded with forceps, and immersed in the nitrating fluid. Nitration continued at 15° for thirty minutes, the flask being shaken occasionally to ensure thorough mixing. A thirty minute reaction time was chosen to conform to that often used in commercial manufacture, and the temperature of 15° was such as to reduce degradation and side reactions (26), yet still allow maximum nitration to take place during the half hour. The liquor was removed by filtration with suction through a coarse, sintered-glass funnel of suitable size, the residual nitrocellulose squeezed slightly to remove excess fluid, and then thrown, piece by piece, with quick stirring, into 250 ml. of a 1:1 mixture (by weight) of ethanol and water (27) previously cooled to -15°. The liquid was again filtered from the solid by suction, through a sintered-glass funnel, into the same suction flask (which had been emptied and washed with water to prevent explosion resulting from the addition of ethanol to nitrating solutions) and the solid squeezed from excess liquid. Two more such washings with 100 ml. volumes of cold, aqueous ethanol were followed by four similar immersions in the same ethanol-water mixture at room temperature to ensure complete removal of the free acids (litmus test).

The washed cellulose nitrate was subsequently boiled three times in succession, for periods of five minutes each, in 100 ml. volumes of 1:1 ethanol-water solution, previously heated to boiling, in order to stabilize the product. Such treatment is reported to remove any bound sulphuric acid and to yield a thoroughly stable nitrocellulose (27, 34, 47). The hot liquid was removed as before, and the ester then dried over phosphoric anhydride and calcium chloride under vacuum, the drying agent being changed as often as necessary until no further liquifaction of the anhydride occurred. It was then deemed suitably dry for subsequent analyses, and was stored in a desiccator over phosphorus pentoxide.

The technical nitrocelluloses thus obtained were colorless and fibrous, but the texture had a more brittle character than was shown by the original cellulose, suggesting the occurrence of degradation during nitration.

## 2. Nitrations With Phosphoric Anhydride-Nitric Acid Mixtures

Nitration without degradation was accomplished by the use of phosphoric anhydride and 100 per cent nitric acid (27, 48) prepared by distillation of a mixture of concentrated sulphuric and concentrated

nitric acids (1:1) in an all-glass apparatus. A 22% mixture (by weight) of phosphoric anhydride in this nitric acid was made by cooling the acid in a glass-stoppered bottle to -15° and adding the anhydride in small portions with shaking and further cooling till the required amount of pentoxide had been consumed. The preparation covered a period of four to six hours, when five hundred ml. of nitric acid was involved, depending upon the efficiency of the cooling mechanism. Attempts to hasten the addition brought about evolution of brown fumes, especially at higher temperatures. The nitration mixture, at first opaque and obviously containing solid anhydride, remained at 0° for one week, whereupon it became a clear, homogeneous liquid. This change in physical state is most important, for unless it has occurred, a nitration to only about 13% N is possible (44). No difficulty in obtaining 13.8 - 14.0% nitrogen content was encountered if solution of the phosphorus pentoxide was complete.

The nitrating liquid, 100 g., was put into a dried, glass-stoppered Erlenmeyer flask, and the flask and contents brought to 15°, whereupon 1 g. (weighed to the second decimal place) of dried, prepared cellulose was added. The reaction was allowed to continue at 15° for thirty minutes. Berl suggests that reaction is completed in the first

five minutes by this powerful mixture (27), but the longer time was allowed so as to be comparable to that used in the technical nitration for the industrial manufacture of guncotton. Removal of the acids, drowning, washing, stabilization, drying and storing of the cellulose nitrate proceeded in exactly the same fashion as in the preparation of the technical nitrates. A colorless, fibrous material of uniform texture, showing no traces of degradation or tendency towards brittleness, was obtained.

## D. ANALYSES FOR NITROGEN (BY SEMI-MICRO KJELDAHL)

Nitrogen analyses were made by a modification of the Gunning method for the determination of nitrogen (49). The sample of dried cellulose nitrate, 0.1 g., was weighed rapidly on a balance, using a cigarette paper as a convenient means of weighing and transferring the guncotton samples. The nitrocellulose slowly absorbs water from the atmosphere, the resulting increase in weight being much greater and much more rapid for the technical nitrates than for the trinitrate. The sample was then transferred to a 250 ml. Kjeldahl flask and 0.3 g. salicylic acid and six ml. concentrated sulphuric acid were added. As some nitrocellulose may adhere to the cigarette paper it was found best to weigh the cigarette paper after the nitrocellulose had been trans-

ferred from the paper into the Kjeldahl flask.

After one to two hours of digestion at room temperature, the solids were found to be completely dissolved. Sodium thiosulphate, 0.8 g., was then added and the mixture warmed gently over a low flame for about five minutes, whereupon 2.0 g. of powdered potassium sulphate and a tiny pinch of selenium catalyst was inserted. The mixture was then gently heated under a hood, until the evolution of gases became less pronounced, and then was heated more strongly till the liquid was clear and colorless. The cooled, viscous liquid was diluted with 100 ml. of distilled water and then made definitely basic by the addition of 50 ml. of 40% sodium hydroxide solution. A small piece of zinc in the flask prevented bumping while the ammonia, with about 75 ml. of water, was distilled into 30 ml. of 4% aqueous boric acid solution containing ten drops of a mixed indicator (50). The ammonia in the boric acid solution was titrated directly with 0.05 N. hydrochloric acid (with a mixed indicator) and the per cent nitrogen calculated by use of the following equation:

$$\%N = \frac{\text{Volume in ml. of HCl}}{1000} \times \frac{N}{x} \times 14.01$$

where N = normality of HCl

and x = weight of sample of cellulose nitrate.

The 4% boric acid solution was prepared by adding the required amount of solid boric acid to prev-

iously boiled, distilled water and after complete solution, was again boiled to eliminate the last traces of carbon dioxide. Any decrease in the volume was made up by the addition of boiled water. It was then stored in a pyrex flask for use. The mixed indicator consisted of 10 ml. of a 0.1% solution in ethanol of brom cresol green added to 2 ml. of a 0.1% solution in ethanol of methyl red (50). Each solution of boric acid, containing the ammonia, was titrated to the disappearance of the greenish color and the first faint appearance of red. The blank was determined in exactly the same way and was applied as a correction for all determinations. Good checks in the duplicate or triplicate analyses were usually obtained in all cases.

## E. DETERMINATION OF INTRINSIC VISCOSITIES

The viscosities were measured with an Ostwald capillary viscosimeter. About 0.05 g. of the dry cellulose nitrate was weighed out carefully and quickly to the fifth place. The nitrate was then added to a weighed amount (100 ml.) of freshly distilled butyl acetate (b.p. 125-127°at 760 mm.) in a glass-stoppered container. Mechanical shaking was continued till a homogeneous solution was obtained. The time for solution varied, but as a rule shaking was continued

for about thirty hours. A few tiny, insoluble, threadlike bodies were observed in all solutions even after prolonged shaking. These bodies were allowed to settle before measurements were made, and were found to have no effect on the time of flow. Approximately, a twenty ml. aliquot portion, (weighed to the fourth place), of the butyl acetate solution, was transferred to a glass tube, closed at one end, and with a ground glass joint at the other end, with dimensions approximately 1" by 8", and capacity about 30 to 40 ml. was found to be suitable. A 5 ml. aliquot of the solution in the glass tube was pipetted into a clean, dry, ostwald viscosimeter, which was then suspended in a water bath at $25^{\circ} \pm 0.1^{\circ}$. After an interval of five minutes, during which time the apparatus reached the temperature of the bath, the small bulb in the instrument was filled with solution by gently exerting pressure on the surface of the liquid in the other arm of the viscosimeter by means of a rubber bulb. This technique minimized evaporation, which inevitably accompanies suction. Times of flow, 70 to 110 secs., were measured with a stop-watch reading to one tenth of a second. An average of at least five readings was taken as the time of flow. Relative viscosities were taken in these dilute solutions as proportional to the time of flow. The quotient of the specific viscosity,

$\eta sp$ or $\eta rel. -1$, by the per cent concentration by weight of the solution was then calculated. The remainder of the original solution was weighed and then diluted with 5 ml. of butyl acetate, and, after a few moments' shaking to allow thorough mixing, weighed again. From these weights, the amount of the solvent and the amount of residual nitrocellulose could be calculated (by aliquots) and the concentration of the cellulose nitrate, in the diluted solution, estimated. Viscosity measurements were repeated on this solution and $\frac{\eta sp}{c\%}$ again calculated. Dilution was continued in the above manner until the numerical value of $\frac{\eta sp}{c\%}$ became constant, and was thereupon considered to be equal to the Intrinsic Viscosity, $[\eta]$ . With the method of using aliquots, as previously outlined, three to five dilutions were usually sufficient to obtain this constant value. Duplicate or triplicate determinations were always made to verify observations. All butyl acetate residues were recovered by fractional distillation.

An example of the calculation is shown below:

(a) Weight of cellulose nitrate = 0.02182 g.

Weight of butyl acetate = 104.08 g.

Weight of aliquot of butyl acetate = 15.76 g.

Weight of nitrate in aliquot portion of butyl acetate $= \frac{15.76}{104.08} \times .02182 = .003306$ g.

Average time of flow (10 runs) of butyl acetate = 71.3 sec.

Average time of flow of butyl acetate nitrate = 87.8 sec.

$$\eta_{sp} = \frac{87.8}{71.3} - 1 = 0.231$$

$$C\% = \frac{0.003306 \times 100}{15.76}$$

$$\frac{\eta_{sp}}{C\%} = \frac{0.231 \times 15.76}{.003306 \times 100} = 11.01$$

(b) Weight of butyl acetate solution after 5 ml. aliquot withdrawn from the 15.76 g. aliquot = 11.36 g.

Weight of butyl acetate solution after adding butyl acetate to make up for volume previously taken out = 16.61 g.

Weight of nitrate left after 1 st. aliquot withdrawn = $\frac{11.36}{15.76} \times 0.003306 = 0.002383$ g.

Average time of flow (10 runs) of butyl acetate solution = 82.4 sec.

$$\eta_{sp} = \frac{82.4}{71.3} - 1 = 0.155$$

$$\frac{\eta_{sp}}{C\%} = \frac{0.155 \times 16.61}{0.002383 \times 100} = 10.80$$

This procedure was repeated until $\frac{\eta_{sp}}{C\%}$ became constant and the average of the last values, which agreed closely, was taken as $[\eta]$.

e.g. $\frac{\eta sp}{C\%}$ for (C) = 10.45

$\frac{\eta sp}{C\%}$ for (d) = 10.44

$\therefore [\eta] = 10.44$

F. OXIDATIONS WITH LEAD TETRAACETATE

Pure, dry ethyl acetate was prepared according to the directions given by Fieser (54) in which commercial ethyl acetate was washed three times with an equal volume of 5% aqueous sodium carbonate ( to remove acetic acid). The ethyl acetate was then washed three times with the same quantity of saturated calcium chloride solution to remove the ethanol which might be present as an impurity. The washed ethyl acetate was dried overnight with anhydrous potassium carbonate, then for three hours with phosphoric anhydride, from which it was then decamted and fractionally distilled twice under anhydrous conditions.

Two liters of acetic acid were freed from aldehyde by heating for two hours under reflux with 10 g. of chromic anhydride, after which time additional chromic anhydride, in small quantities, was inserted and the acetic acid refluxed until oxidation of all aldehydes had taken place. (No further change of colour of chromic anhydride after refluxing). The addition of too large a quantity of chromic anhydride was avoided as it might react violently with the impure acetic acid. The acid was then purified by fractionation in

an all-glass apparatus (41, 55), acetic anhydride was purified by careful fractionation of the stock material.

A good grade of lead tetraacetate was made by the procedure of Hockett and McClenahan (56, cf. also 57, 58). A mixture of 530 ml. of purified glacial acetic acid and 115 ml. of acetic anhydride was heated to 75° in a 1-liter, 3-necked, round-bottom flask, fitted with a thermometer and a mechanical stirrer. Dry red lead, 150 g., was added in 15 g. portions, each successive addition being made only when the color of the oxide previously added had vanished. At the end of the reaction, wherein the temperature had been maintained below 90°, the faintly red solution, now practically free of unreacted lead oxide, was allowed to cool in the stoppered flask, whereupon the remaining traces of color disappeared, and the lead tetraacetate crystallized out in long, colorless needles. The acetate was then separated from the liquid by filtration with gentle suction, and washed four times with small portions of cold purified glacial acetic acid. A 0.1 N acetic acid solution of the lead tetraacetate solution was immediately prepared. The dry lead tetraacetate darkens rapidly if exposed to water vapor in the air. Any color, caused by contact of the salt with water vapor in the air, might be removed by solution of the solid in hot glacial acetic acid,

decolorization with norite if necessary, and then recrystallization.

The strength of the acetic acid solution of the lead tetraacetate was determined by pipetting 20 ml. of the liquid into 30 ml. of a sodium acetate buffer (consisting of 20 g. potassium iodide plus 250 g. sodium acetate per liter of aqueous solution) and titrating the liberated iodine to a starch end point with 0.02 N sodium thiosulphate (59, 41).

About 0.5 gm. of the prepared nitrocellulose, previously dried for twenty four hours under vacuum over phosphoric anhydride, was placed on a cigarette paper and the two were weighed (to five decimal places). The sample of guncotton was then transferred into a 200 ml. glass-stoppered volumetric flask. The paper was now weighed and the weight of the nitrate determined. The solid was covered with 125 ml. of purified, anhydrous ethyl acetate, and slowly dissolved by agitation on a mechanical shaker, whereupon 50 ml. of 0.1 N glacial acetic acid solution of lead tetraacetate was added, followed by enough anhydrous ethyl acetate to bring the total volume to the 200 ml. mark. The flask was shaken to ensure a homogeneous solution. Two blank determinations were carried out simultaneously. Oxidation was carried out at 25° (±0.1°). Consumption of the lead tetraacetate by the cellulose nitrate was

determined by the potassium iodide-sodium thiosulphate method of Dimroth and Schweitzer (59). At suitable intervals the volumetric flasks were removed from the bath, shaken briskly and then put back in the bath. After allowing any suspended undissolved nitrocellulose to settle (a few minutes), 10 ml. aliquots were pipetted into 30 ml. of potassium iodide-sodium acetate solution (41) contained in a 250 ml. Erlenmeyer flask. Eleven ml. of pure ethyl acetate was placed in a 20 ml. Erlenmeyer flask and the drained pipette was filled, by suction, with ethyl acetate. This solution was also pipetted into the 250 ml. Erlenmeyer flask. By this method of flushing the pipette most of the adhering oxidation solution is removed and more reproducible results are thus obtained. This is particularly important since the viscosity of the solutions of cellulose nitrate in ethyl acetate varies with the nitrogen content of the guncottom. 75 ml. of water was added and the solution was then titrated with 0.02 N sodium thiosulphate until the colour of the solution had changed to a light yellow, whereupon 3 ml. of starch solution was added, and titration then completed. The titration was slow, and required considerable agitation of the flask to allow all the iodine in the ethyl acetate layer to come into intimate contact with the thiosulphate in the water layer. Near the end point, after the addition of each drop, the flask had to be shaken for

a time, since the darkening due to the starch indicator reappeared very slowly. A colorless liquid denoted the completion of the titration. Consumption of oxidant was expressed as the difference in titrations between the blanks and the sample.

An example of the calculation follows:

Weight of cellulose nitrate = 0.50020 g.

Volume of $Na_2S_2O_3$ used by 10 ml. aliquot from blanks (average) = 9.80 ml.

Volume of $Na_2S_2O_3$ used by 10 ml. aliquot after oxidation = 8.98 ml.

Consumption of $Na_2S_2O_3$ by 10 ml. aliquot of cellulose nitrate solution = 0.82 ml.

Consumption of $Na_2S_2O_3$ by 200 ml. of cellulose nitrate solution = 16.40

Normality of $Na_2S_2O_3$ = 0.02787

Moles of oxidant consumed by sample = $\frac{0.02787 \times 16.40}{1000}$

Moles of oxidant consumed per glucose unit

$$= \frac{.02787 \times 16.40}{1000} \times \frac{162}{0.50020} = 14.80 \times 10^{-2} \text{ moles.}$$

Each sample of nitrocellulose was oxidized for a period of approximately one thousand hours. The results of the oxidations are compiled in Tables VI and VII pp. 61 and 63 , and in Fig. 10 p. 95 .

At a later date a portion of the same cotton linters was used in the preparation of another series of

nitrocelluloses having nitrogen contents varying from 9.46 to 9.94%. This is indicated in Table VIII p.64, and Fig. 11 and 12 on pages 98 and 99 respectively. The conditions of nitration used in the preparation of samples $S_o$ and $S_{10}$ were identical.

TABLE VI

LEAD TETRAACITATE OXIDATIONS[a] OF TECHNICAL NITROCELLULOSES[b]

| Sample Ro Oxidation time in hours | Consumption[c] of oxidant in miles X $10^{-2}$ per glucose unit | Sample $R_1$ (11.09%N) Oxidation time in hours | Consumption[c] of oxidant in moles X $10^{-2}$ per glucose unit |
|---|---|---|---|
| 4.6 | 3.57 | 25 | 1.62 |
| 28 | 3.57 | 103 | 5.00 |
| 79 | 5.62 | 149 | 7.08 |
| 125 | 7.61 | 192 | 8.36 |
| 184 | 10.5 | 243 | 9.66 |
| 252 | 11.4 | 317 | 12.40 |
| 305 | 11.7 | 364 | 13.67 |
| 351* | 11.8 | 440 | 14.70 |
| 571 | 14.2 | 529.4 | 16.12 |
| 738.2 | 18.2 | 656.9 | 17.38 |
| 765.3 | 18.3 | 772.5 | 19.06 |
| 853.1 | 18.9 | 922.1 | 21.2 |
| 978.1 | 19.7 | | |
| 1242.1 | 23.1 | | |

[a] Oxidized with 0.1N $Pb(OAc)_4$ in ethyl acetate at $25^{\circ} \pm 0.01^{\circ}$

[b] Dry cotton linters soaked in water and dried directly in air. Samples stored over concentrated $H_2SO_4$, and subsequently nitrated with $HNO_3$-$H_2SO_4$-$H_2O$ mixture. $HNO_3$ = 41.4%; $H_2SO_4$ = 39.7%; $H_2O$ = 18.9%

[c] Average of duplicate estimations that were in good agreement.

TABLE VI (Continued)

LEAD TETRAACETATE OXIDATIONS OF TECHNICAL NITROCELLULOSES

| Sample $R_5$ (11.15% N) | | Sample $R_{17}$ (11.36% N) | |
|---|---|---|---|
| Oxidation time in hours | Consumption of oxidant in moles X $10^{-2}$ per glucose unit | Oxidation time in hours | Consumption of oxidant in moles X $10^{-2}$ per glucose unit |
| 23 | 2.48 | 25 | 1.21 |
| 74 | 5.76 | 75 | 3.64 |
| 119 | 5.41 | 117.5 | 4.90 |
| 194 | 7.82 | 169 | 6.76 |
| 242 | 9.51 | 233.4 | 7.30 |
| 284 | 10.02 | 289.7 | 8.28 |
| 336 | 11.52 | 362.8 | 9.26 |
| 405 | 12.50 | 451.3 | 11.10 |
| 457 | 13.48 | 575.0 | 12.62 |
| 531 | 15.18 | 690.5 | 15.05 |
| 620.5 | 16.64 | 819.6 | 17.30 |
| 744.1 | 18.37 | | |
| 859.7 | 19.80 | | |
| 1000.9 | 22.30 | | |

TABLE V11

LEAD TETRAACETATE OXIDATION[a] OF NITROCELLULOSE[b]

Sample P (13.80% N)

| Oxidation time in hours | Consumption of oxidant in moles X $10^{-2}$ per glucose unit |
|---|---|
| 20.7 | 2.40[c] |
| 74 | 0.41 |
| 116 | 0.95 |
| 195 | 0.47 |
| 240 | 1.34 |
| 284 | 1.00 |
| 335 | 1.35 |
| 533.3 | 0.72 |
| 745.3 | 0.98 |
| 1011.3 | 0.54 |

[a]Oxidized with 0.1N $Pb(OA_c)_4$ in ethyl acetate at $25^{\circ} \pm 0.01^{\circ}$

[b]Cotton linter nitrated with a $HNO_3$-$P_2O_5$ mixture.

[c]In error pipette not flushed.

TABLE VIII

LEAD TETRAACETATE OXIDATIONS[a] OF TECHNICAL NITROCELLULOSES[b]

| Sample $S_0$ (9.72%N) | | Sample $S_{10}$ (9.94%N) | |
|---|---|---|---|
| Oxidation time in hours | Consumption of oxidant in moles X $10^{-2}$ per glucose unit | Oxidation time in hours | Consumption of oxidant in moles X $10^{-2}$ per glucose unit |
| 41.0 | 3.60 | 42.3 | 3.74 |
| 118 | 10.42 | 118.7 | 9.87 |
| 162.3 | 13.47 | 163.7 | 12.70 |
| 214.6 | 15.82 | 216.5 | 15.29 |
| 286.8 | 19.99 | 288.4 | 19.39 |
| 336.4 | 22.20 | 338.0 | 21.17 |
| 401.9 | 26.10 | 404.0 | 24.78 |

[a] Oxidized with 0.1N $Pb(OAc)_4$ in ethyl acetate at $25^{\circ} \pm 0.01^{\circ}$

[b] Cotton linters nitrated with a $HNO_3$-$H_2SO_4$-$H_2O$ mixture.

$HNO_3$ = 39.5%; $H_2SO_4$ = 38.8%; $H_2O$ = 21.7%

TABLE VIII (Continued)

LEAD TETRAACETATE OXIDATIONS OF TECHNICAL NITROCELLULOSES

| Sample $S_1$ (9.46%N) | | Sample $S_{17}$ (9.92%N) | |
|---|---|---|---|
| Oxidation time in hours | Oxidant in moles X $10^{-2}$ per glucose unit | Oxidation time in hours | Oxidant in moles X $10^{-2}$ per glucose unit |
| 41.3 | 3.79 | 42.6 | 3.72 |
| 118.1 | 11.56 | 119.0 | 9.81 |
| 162.6 | 14.80 | 164.0 | 12.55 |
| 214.8 | 17.74 | 216.8 | 15.40 |
| 286.9 | 22.90 | 288.8 | 20.18 |
| 336.5 | 25.60 | 338.1 | 22.48 |
| 402.0 | 30.12 | 404.0 | 26.98 |

## RESULTS AND DISCUSSION

Dewaxed cotton linters (Sample V) when alternately wetted with water and dried sharply over phosphoric anhydride under vacuum prior to storing over concentrated sulphuric acid showed a progressive increase in accessibility to thallous ethylate in ether (21) proportional to the number of wetting-drying cycles (Table IX page 70 , Fig. 5 page 68 ). Seven such cycles raised the accessibility by approximately 2/3 (0.30% to 0.49%). This increased accessibility is also reflected in a corresponding improvement in the degree of nitration. A standard sulphuric acid-nitric acid-water nitrating mixture (46) gave 11.04% N with untreated dewaxed linters as against 11.49% N with the linters having received seven wetting-drying treatments (Sample V, Table IX page 70 and Fig. 6 page 69).

A second portion of dewaxed cotton linters (Sample W) was given similar cyclic wetting and drying treatments but with removal of water achieved by air drying rather than by phosphorus pentoxide before storage over concentrated sulphuric acid. Here again twelve cycles is associated with an increase from 1104% to 11.55 % nitrogen (Table X page 74 ).

In order to check these results as well as to

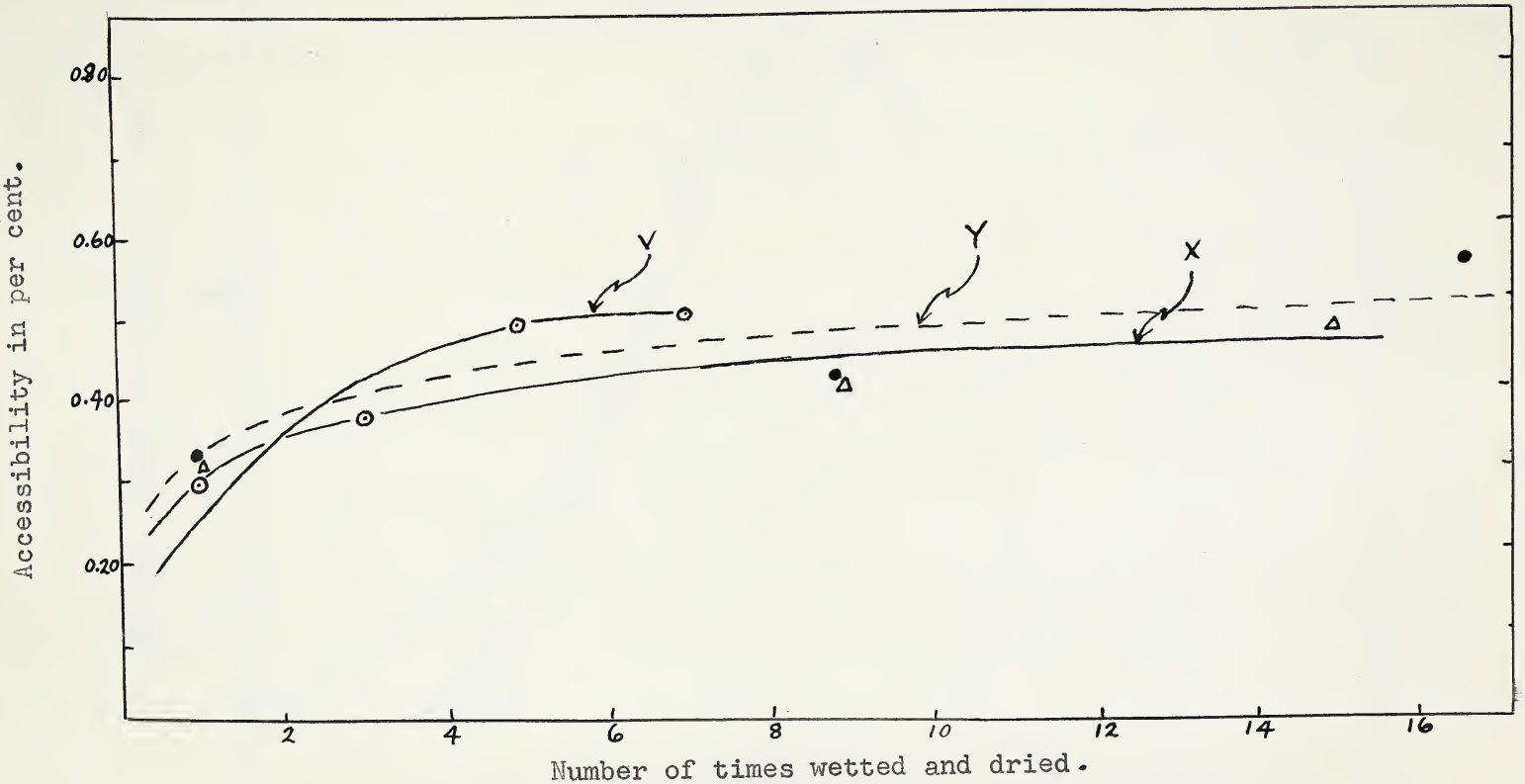



Fig. 5.- Accessibilities of cotton linters cyclically wetted with water and dried.

V⊙ Dried over $P_2O_5$ under vacuum and stored over conc. $H_2SO_4$.

X△ Dried in air, then over $P_2O_5$ under vacuum, and stored over conc. $H_2SO_4$.

Y● Dried in air and stored over conc. $H_2SO_4$.

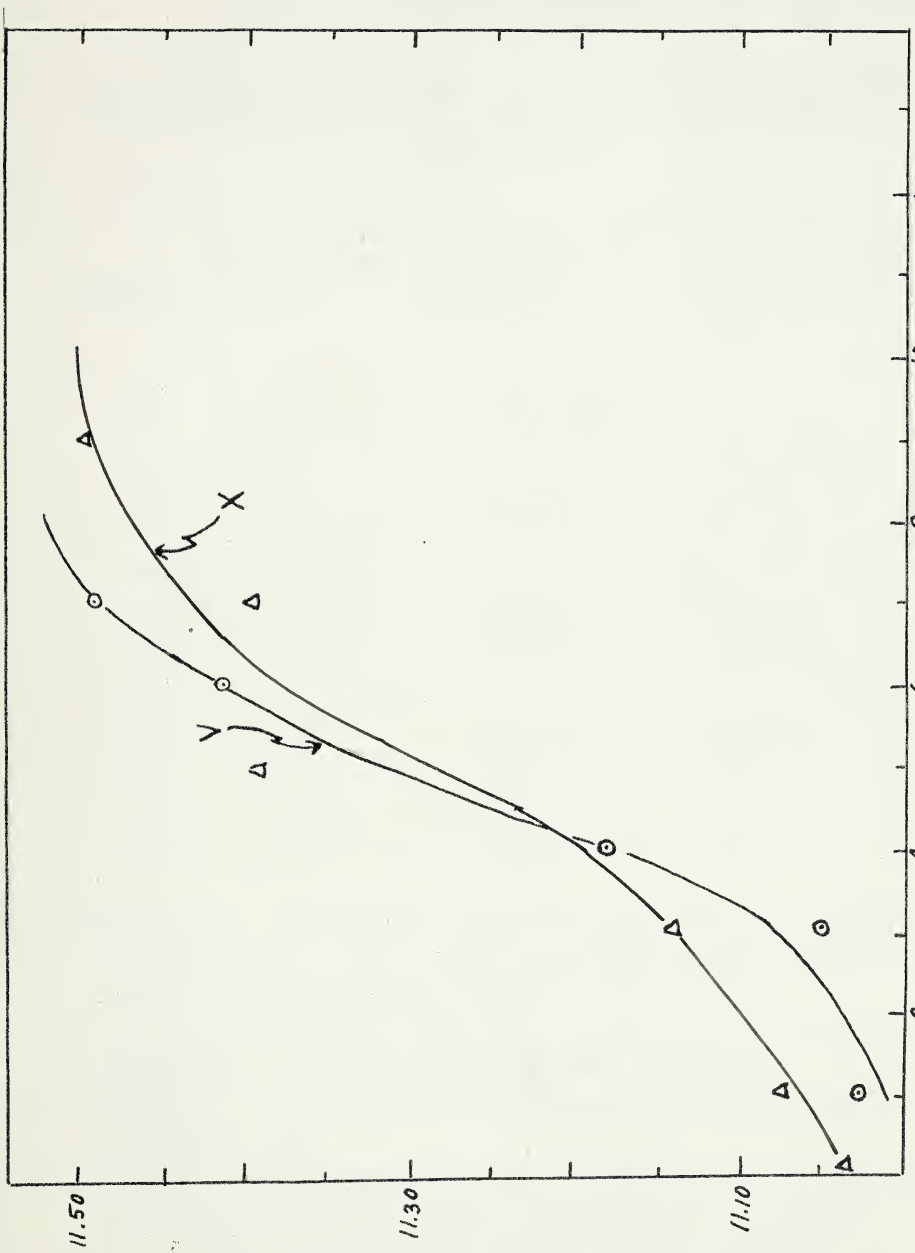



Fig. 6.- Nitrogen contents of nitrates of cotton linters cyclically wetted with water and dried.
V ⊙ - Dried over $P_2O_5$ under vacuum.
X △ - Dried in air, then over $P_2O_5$ under vacuum.

TABLE IX

NITROGEN AND VISCOSITY MEASUREMENTS ON CELLULOSE NITRATES FROM COTTON LINTERS CYCLICALLY WETTED AND DRIED[a]

(Each sample dried over $P_2O_5$ under vacuum and stored over conc. $H_2SO_4$

| Sample | No. of times soaked and dried[a] | Accessibility[b] of the dried cellulose % | Nitrogen[c] content of the nitrate % | Viscosity[d] of the nitrate |
|---|---|---|---|---|
| (1) | (2) | (3) | (4) | (5) |
| $V_o$ | 0 | - | 11.04 | - |
| $V_1$ | 1 | 0.30 | 11.03 | 11.40 |
| $V_2$ | 2 | - | 11.00 | - |
| $V_3$ | 3 | 0.38 | 11.05 | - |
| $V_4$ | 4 | - | 11.18 | 11.28 |
| $V_5$ | 5 | 0.49[e] | 11.22 | - |
| $V_6$ | 6 | - | 11.41 | - |
| $V_7$ | 7 | 0.49 | 11.49 | 10.55 |

[a]Twenty g. of dewaxed cellulose was soaked in distilled water for 12 hours, then dried over $P_2O_5$ under vacuum. Samples $V_2$ to $V_7$ each soaked in water for 3 hours.

[b]% methoxyl content of methylated cellulose multiplied by 100/57.4. Average of triplicate analyses.

[c]Average of duplicate or triplicate estimations agreeing within $\pm$ 0.1%.

[d]Average of triplicate or duplicate estimations agreeing to within $\pm$ 0.1. In n-butyl acetate at $25^\circ \pm 0.01^\circ$.

[e]Individual values were 0.38%; 0.44%; 0.66%.

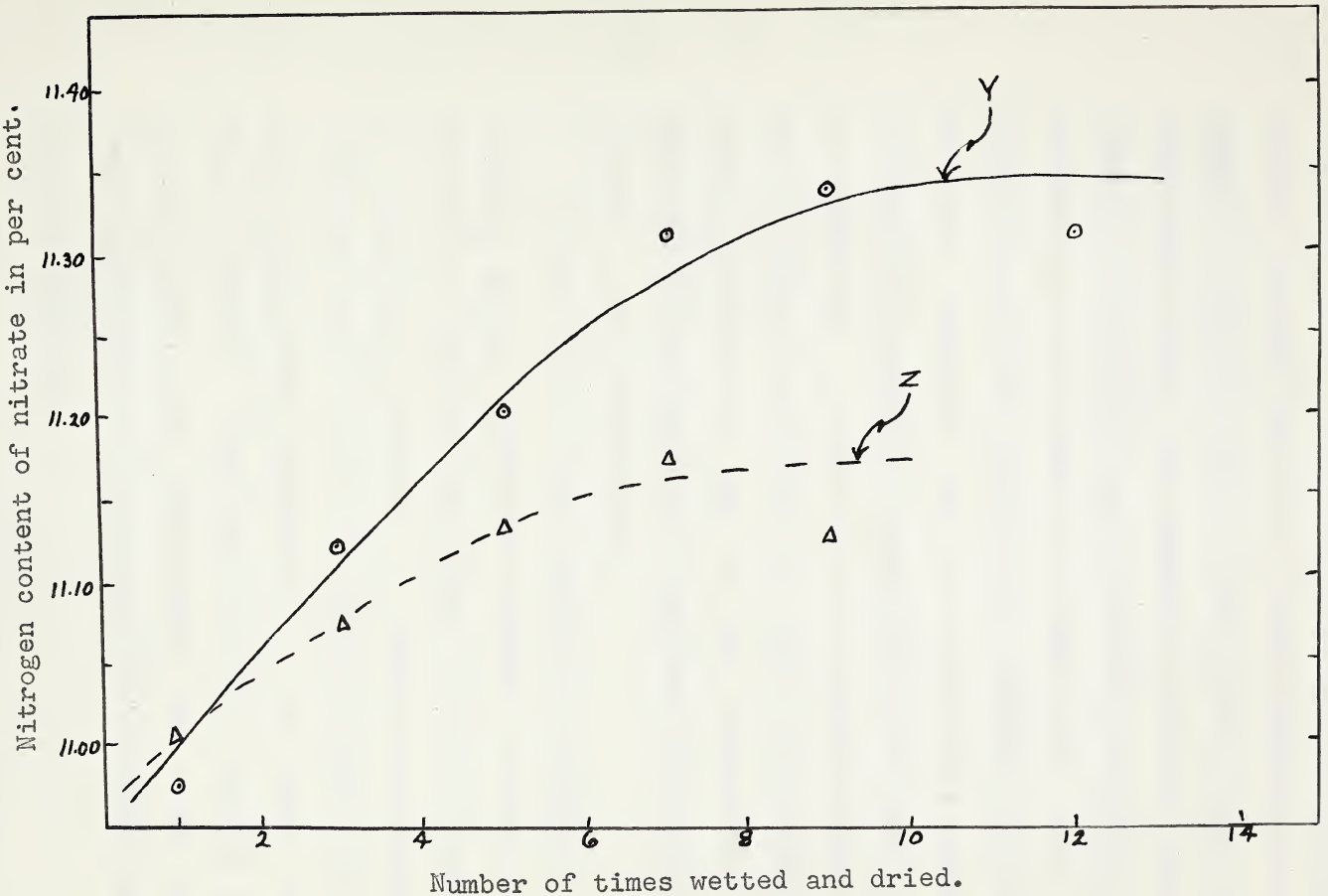



Fig. 7. - Nitrogen contents of nitrates of cotton linters cyclically wetted with water and dried.

$Y^{\odot}$ - Dried in air and stored over conc. $H_2SO_4$.

$Z^{\Delta}$ - Dried in air and stored with no drying agent.

discover whether there is a limit to the increase of accessibility of cotton linters due to wetting-drying cycles, two more samples of cotton linters were prepared. Sample X (Table XI, page 75) was given fifteen cycles with sharp drying over phosphorus pentoxide whereas Sample Y (Table XII, page 76) received seventeen such treatments with air-drying at each cycle. Both X and Y were stored over concentrated sulphuric acid before analysis. Table XI, page 75, reveals that sample X suffered an increase of accessibility of from 0.32% to 0.48% (Fig. 5, page 68) with a parallel improvement in ease of nitration (11.08% to 11.50% Nitrogen). Sample Y (Table XII, page 76) also corroborated the previous observations by an increased accessibility (10.96% to 11.31% Nitrogen).

In all cases sharper drying is accompanied by slightly greater increases in degree of nitration. Moreover, a limit to the effects of wetting drying on the extent of nitration is indicated for Sample X (Table XI, page 75) and for Sample Y (Table XII, page 76) more clearly shown graphically in Fig. 6, page 69 and Fig. 7, page 71. This limit is not as clearly indicated in the accessibility measurements, due to the fact that such small values for accessibilities entail inaccuracies of 10 to 15% (21).

Concurrently, another portion of dewaxed cotton

linters (Sample Z) was given seven alternate wetting and air drying treatments similar to those of Sample Y and then was stored in a desiccator with no drying agent. When each portion of Sample Z was subsequently nitrated by a standard technical mixture, an overall increase of 0.17% N was observed (Table XIII, page 79, Fig. 7, page 71). In this case also a progressive increase in degree of nitration parallels the increase in the number of wetting and air drying cycles. Apparently storage of all samples, prior to nitration, over a desiccant (concentrated sulphuric acid) produces a more pronounced difference in nitration (cf. Sample Z and Sample Y). However one should not consider that this enhanced effect, due to intense drying, is necessarily of general application since there is a considerable variation in increase of accessibility due to definite number of wetting drying cycles even with the linters from the same source (See Table XIV, page 80). It is also interesting to note that the nitrocelluloses obtained from the all air-dried cellulose (Sample Z, Table XIII) were more uniform than those of the more rigorously dried linters (Samply Y, Table XII) since the Kjeldahl nitrogen triplicate analyses of the former diverged from their mean by not more than ± 0.04%, whereas those of the latter diverged from their mean by ± 0.1%.

A series of nitrating mixtures calculated to produce

TABLE X

NITRATIONS OF SWOLLEN COTTON LINTERS CYCLICALLY WETTED AND DRIED

(Each sample soaked in water, dried in air, and stored over conc. $H_2SO_4$)

| Sample | No. of times soaked and dried | Nitrogen[b] content of the nitrate % |
|---|---|---|
| W 0 | 0 | 11.04 |
| W 1 | 1 | 11.08 |
| W 6 | 6 | 11.28[a] |
| W 12 | 12 | 11.55 |

[a] Individual values were 11.21; 11.20; 11.44.

[b] Average of triplicate estimations agreeing within ± 0.1%

TABLE XI

NITROGEN AND VISCOSITY MEASUREMENTS ON CELLULOSE NITRATES FROM COTTON LINTERS CYCLINCALLY WETTED AND DRIED[a]

(Each sample dried over $P_2O_5$ under vacuum, then stored over conc. $H_2SO_4$)

| Sample | No. of times soaked and dried[a] | Accessibility[b] of the dried cellulose % | Nitrogen[c] content of the nitrate % | Viscosity[d] of the nitrate [η] |
|---|---|---|---|---|
| (1) | (2) | (3) | (4) | (5) |
| X 0 | 0 | ---- | 11.04 | ----- |
| X 1 | 1 | 0.32 | 11.08 | 10.83 |
| X 3 | 3 | ---- | 11.14 | ----- |
| X 5 | 5 | ---- | 11.40 | 10.50 |
| X 7 | 7 | ---- | 11.40 | ----- |
| X 9 | 9 | 0.41 | 11.50 | 9.92 |
| X15 | 15 | 0.48 | ----- | ----- |

[a] Twenty g. of dewaxed cellulose was soaked in distilled water for 12 hours, then dried over $P_2O_5$ under vacuum. Remaining samples each soaked in water for 3 hours.

[b] % methoxyl content of methylated cellulose multiplied by 100/57.4. Average of duplicate analyses agreeing within ± 0.02%

[c] Average of duplicate or triplicate estimations agreeing within ± 0.1%

[d] Average of duplicate estimations agreeing to within ± 0.07. In n-butyl acetate at 25° ± 0.01°.

TABLE XII

NITROGEN AND VISCOSITY MEASUREMENTS ON CELLULOSE NITRATES FROM COTTON LINTERS CYCLICALLY WETTED AND DRIED

(Each sample dried in air and stored over conc. $H_2SO_4$).

| Sample | No. of times soaked and dried[a] | Accessibility[a] of the dried cellulose % | Nitrogen[b] content of the nitrate % | Viscosity[c] of the nitrate $[\eta]$ |
|---|---|---|---|---|
| (1) | (2) | (3) | (4) | (5) |
| Y 1 | 1 | 0.33 | 10.96 | 10.42 |
| Y 3 | 3 | ---- | 11.12 | ----- |
| Y 5 | 5 | ---- | 11.20 | 9.81 |
| Y 7 | 7 | ---- | 11.31 | ----- |
| Y 9 | 9 | 0.41 | 11.34 | ----- |
| Y 12 | 12 | ---- | 11.31 | 9.47 |
| Y 17 | 17 | 0.56 | ----- | ----- |

[a] % Methoxyl content of methylated cellulose multiplied by 100/57.4. Average of duplicate estimations agreed to within ± 0.01%.

[b] Average of duplicate or triplicate estimations agreeing within ± 0.1%.

[c] Average of duplicate estimations agreeing to within ± 0.08. In n-butyl acetate at 25° ± 0.01°.

nitrocelluloses varying in degree of substitution from mono to trinitrate (Sample T, Table XIV, page 80, Fig. 8, page 82) all showed the same, typical increase in extent of nitration for a quantity of cotton linters wetted and air-dried seventeen times over the same linters wetted and air-dried only once. The powerful mixture of 100% nitric acid and phosphorus pentoxide showed a 0.22% N increase whereas technical mixtures exhibited greater differences. A correlation might be possible between strength of reagent and magnitude of difference in degree of nitration. The nitric acid-phosphoric anhydride mixture was expected to yield nitrates of the same nitrogen content for all linter samples since it is known to nitrate celluloses, having different accessibilities, to almost the same degree (60).

The data of Tables IX to XIV all serve to corroborate the fact that an improvement in the degree of nitration of cotton linters was brought about by alternately wetting and drying them prior to nitration. Furthermore, the increase in accessibility was proportional to the number of wetting-drying cycles. Beneficial effects of water in improving accessibility and ease of nitration have been observed by other workers. Purves and co-workers (10) found that a cellulose of known percentage accessible surface, when allowed to adsorb only small amounts of water (6% to 9%) underwent further swelling with consequent increase in

accessible surface. Schur and Hoos (12) found that samples of cellulose shredded in water, then dried, and subsequently nitrated, showed a nigher nitrogen content than cellulose shredded in the dry state and subsequently nitrated.

It is very interesting to note that cotton linters, highly swollen with aqueous caustic soda, then dried by solvent exchange, and subsequently collapsed by soaking with water and direct drying, when nitrated with a technical nitrating mixture showed a 0.25% decrease in nitrogen from that obtained by identical nitration of the swollen linters (Table XV, page 85). This decrease in nitrogen content of the nitrate from 11.37 to 11.12% was associated with a decrease in accessibility from 16% to about 0.20%. This work was a corroboration of part of the research done by Brown and Purves (16).

The decrease in nitrating ability found in highly swollen cotton linters collapsed by drying from water is directly in contrast to the increase of nitrogen content shown by nitrated cotton linters which were alternately wetted and dried. However, it must be kept in mind that linters swollen with strong caustic solution, and then treated with water, undergo a change in the crystal lattice of the cellulose (61). A strong alkali solution affects both the crystalline as well as the amorphous regions of the cellulose (60), whereas

TABLE XIII

NITRATIONS OF COTTON LINTERS CYCLICALLY WETTED AND DRIED

(Each sample dried in air and stored in desiccator with no drying agent).

| Sample | No. of times soaked and dried | Nitrogen[a] content of the nitrate % |
|---|---|---|
| $Z_1$ | 1 | 11.00 |
| $Z_3$ | 3 | 11.07 |
| $Z_5$ | 5 | 11.13 |
| $Z_7$ | 7 | 11.17 |
| $Z_9$ | 9 | 11.12[b] |

[a]Average of triplicate estimations agreeing within ± 0.04%.

[b]Nitrating mixture had deteriorated, hence this value can not give a correct comparison of ease of nitration.

TABLE XlV

NITRATIONS OF COTTON LINTERS, CYCLICALLY WETTED AND DRIED, WITH DIFFERENT NITRATING MIXTURES

(Each sample dried in air and finally stored over conc. $H_2SO_4$)

| Nitrating mixture | Composition of mixture in % by weight | | | | Nitrogen[a] content % Sample | | Overall difference in nitrogen content in parallel nitration % |
|---|---|---|---|---|---|---|---|
| | $HNO_3$ | $H_2SO_4$ | $H_2O$ | $P_2O_5$ | $T_1$(1cycle) | T17(17cycles) | |
| Technical[b] #1 | | | | | 7.32 | 7.65 | 0.33 |
| Technical #2 | 39.5 | 38.8 | 21.7 | | 9.46 | 9.92 | 0.46 |
| Technical #3 | 41.4 | 39.7 | 18.9 | | 11.09 | 11.36 | 0.27 |
| $HNO_3$-$P_2O_5$ | 78.0 | | | 22 | 13.77 | 13.99 | 0.22 |

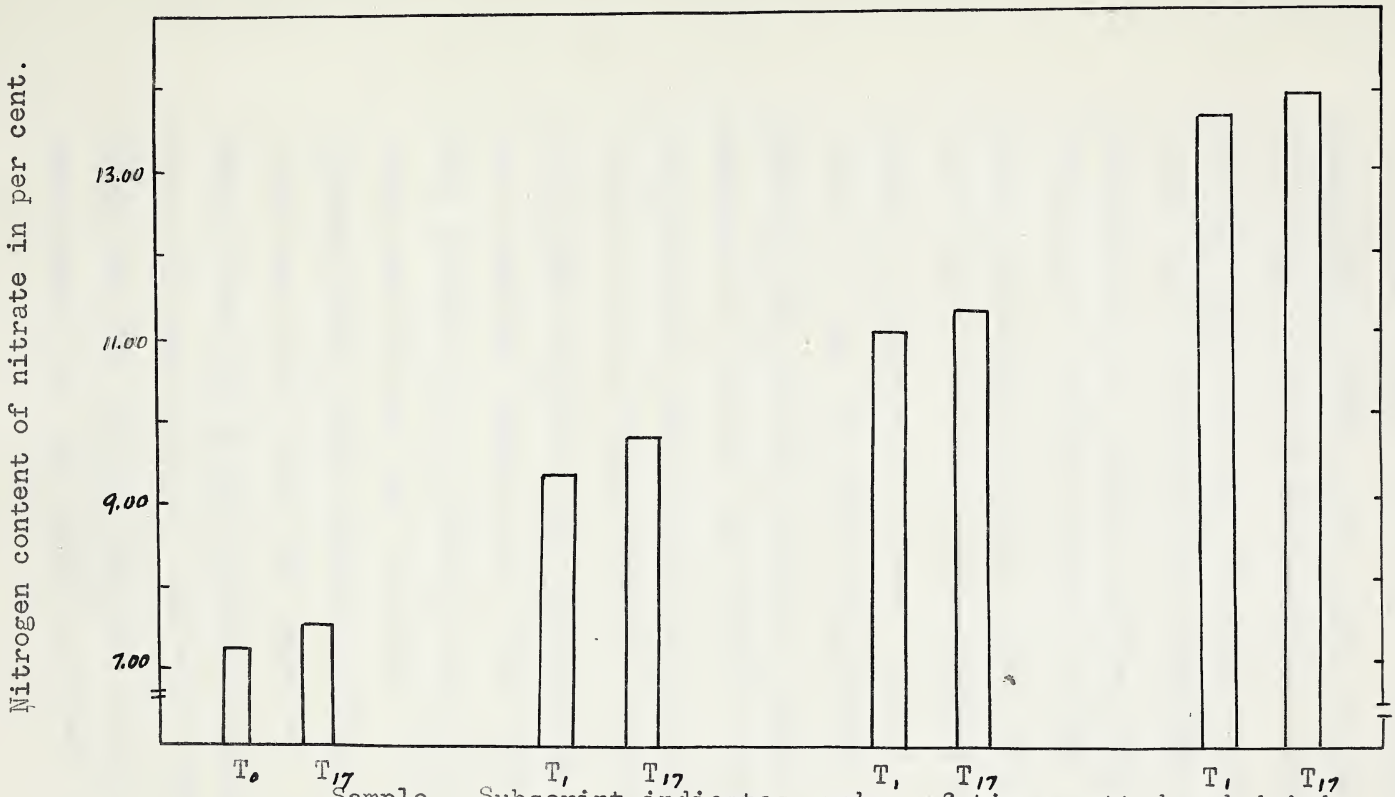
[a]Average of duplicate or triplicate determinations agreeing within ±0.1%.

[b]Not analyzed.

water is believed to affect the amorphous domain chiefly (6).

It is evident that there is a correlation between the wetting drying cycles and the increase in accessibility of the cotton linters. As the changing humidity in the atmosphere provides a situation in which such wetting drying cycles may occur, it was decided to investigate the role of atmospheric conditions in changing the reactivity of cellulose. Accordingly, sets of cellulose samples were exposed to conditions of weathering and storage, and then nitrated to determine the change in reactivity resulting from such treatment (Samples Y and N, Table XVI, page 88). Each set consisted of two samples of linters, differing in the ease of nitration resulting from either a series of wetting-drying treatments (Y) or alkali swelling followed by drying by solvent exchange to maintain increased accessibility and from water to decrease the accessibility (N). All the linters so chosen had already been stored in a closed desiccator for seven months prior to weathering experiments (See Table XVI, page 88).

When samples Y-1-B and Y-15-B (portions of the same cotton linters as Samply Y, Table XII, page 76), which were exposed to atmospheric conditions existing in a heated basement room, were nitrated with a new technical nitrating mixture, the nitrogen content of the nitrate of Y-15-B exceeded that of Y-1-B by 0.23%.




Sample - Subscript indicates number of times wetted and dried.

Fig. 8.- Comparison of extent of nitration by different nitrating mixtures of a sample of dewaxed cotton linters (T), subjected to a series of wetting-drying cycles.

Moreover, Y-15-B gave a nitrate which was non-uniform in nitrogen content as was evidenced by the fact that six nitrogen analyses of it gave individual values of 10.91; 10.96; 11.09; 11.17; 11.27; 11.42%. It is interesting to recall that portions of Samples Y-1 and Y-12 (See Table XII, page 76), which, prior to weathering had been esterified with a different technical nitrating mixture, yielded nitrates which showed a difference in nitrogen content of 0.35%. Samples of highly swollen and collapsed linters (N-1 and N-C-1), which formerly had been used to produce nitrates which showed a difference in nitrogen content of 0.25% (Table XV, page 85), after being weathered in an unheated open shed for December, January and March and subsequently nitrated, gave nitrates which exhibited a difference of only 0.1% in nitrogen content. Samples Y-3-O and Y-9-O, formerly showing an increase of 0.22% in nitrogen content of the corresponding nitrates for the six wetting drying cycles (Table XII, page 76), after weathering in an unheated open shed for December, January and February and subsequent nitration, gave nitrates having almost identical nitrogen content (11.05 and 11.04%, Table XVI, page 88). Similarily, Samples Y-3-D and Y-12-D (formerly differing by 0.19% N, Table XII), were kept in a desiccator over no drying agent, and when nitrated produced nitrates which had approximately the same nitrogen content (10.91 and 10.96%,

Table XVI, page 88). Moreover, the nitrogen content of the nitrate prepared from Sample Y-3-O (which was exposed to outside atmospheric conditions) was 11.05%, whereas that of the same sample, Y-3-D, which was kept in a relatively dry atmosphere during storage was 10.91%. It would, therefore appear that outside storage of dry cotton linters may lead to an improvement in their ease of nitration. It is apparent that the differences in reactivity towards nitrating agents, originally found for the cyclically wetted and dried cellulose, is eliminated by weathering effects.

To determine whether the duration of the water immersion was a controlling factor in attaining increased accessibility of the cellulose, quantities of the dewaxed cotton linters were soaked in distilled water for a period of seventeen days, then dried either in air or over phosphorus pentoxide under vacuum. Portions of these dried samples were given a second soaking for an additional thirty days and again dried as before. No significant difference was found in the degree of nitration obtained (Table XVII, page 92). Apparently the difference in reactivity of the cotton linters is dependent upon the number of wetting and drying cycles rather than upon time of immersion in water.

TABLE XV

NITRATION AND ACCESSIBILITY OF ALKALI SWOLLEN COTTON LINTERS.

| Sample | Accessibility[c] of the dried cellulose % | Nitrogen[d] content of the nitrate % |
|---|---|---|
| 1 - Swollen[a] | 16.4 | 11.37 |
| 11- Collapsed[b] | 0.16 | 11.12 |

[a]Sample swollen with 10% aqueous sodium hydroxide and dried by solvent exchange.

[b]Dry swollen sample soaked in water and dried directly over $P_2O_5$ under vacuum.

[c]% methoxyl content of methylated cellulose multiplied by 100/57.4. Average of triplicate analyses.

[d]Average of triplicate estimations agreeing within $\pm$0.1%.

Moreover, it was very interesting to discover that the nitrocelluloses from cotton linters, which were alternately wetted and sharply dried many times over phosphorus pentoxide under vacuum, showed a greater heterogeneity than nitrocelluloses obtained from cotton linters, wetted similarily, but air dried only prior to storage over concentrated sulphuric acid, or those obtained from linters which were air dried only. This heterogeneity was evidenced by the fact that in the determinations of the nitrogen content of the nitrocelluloses greater deviation from the mean was observed generally in the case of the nitrocelluloses obtained from the more sharply dried samples than from those dried less rigorously.

In order to discover whether any changes in the degree of polymerization of the nitrocellulose had occurred as a result, either directly or indirectly, of the alternate wetting and drying treatments of the cotton linters, viscosity determinations were made of the solutions of corresponding nitrocelluloses in n-butyl acetate. When cotton linters, alternately wetted and sharply dried over phosphorus pentoxide under vacuum for seven cycles prior to nitration (Sample V), were nitrated, the intrinsic viscosity of the correspond- nitrates was lowered by 0.85 (11.40 to 10.55, Table IX, Column 5, page 70 ). Sample X, subjected to eight similar

wetting treatments, but dried in air partially before being dried sharply over phosphorus pentoxide under vacuum, showed a decrease of 0.91 in the intrinsic viscosity of the nitrate (10.83 to 9.92, Table XI, column 5, page 75). It is thus seen that a decrease in viscosity of the nitrate was associated with an increase in the number of wetting-drying cycles. It must be remembered that with the increase in the number of alternate wetting-drying treatments of cotton linters, there was an increase in nitrogen content of the corresponding nitrates (Tables IX and XI, column 4). This decrease in viscosity is, therefore, surprising since an increase in viscosity is generally associated with an increase in degree of substitution of the nitrocellulose (35). Probably the wetting drying cycles made the cotton linters more susceptible to cleavage of the macromolecule during nitration since degradation does occur in technical nitrations (64). Samply Y, cyclically wetted twelve times in a similar way to that employed for Samples V and X, but less rigorously dried (in air and then stored over concentrated sulphuric acid) when nitrated, suffered a decrease of only 0.65 in intrinsic viscosity of the nitrates (Table XII, Column 5, page 76). Sharper drying is apparently accompanied by greater decreases in intrinsic viscosity (Fig. 9, page 90).

In order to become familar with the technique of

TABLE XVI

NITRATIONS[a] OF COTTON LINTERS EXPOSED TO CONDITIONS OF WEATHERING AND STORING[f]

| Sample | Length of weathering in months | Nitrogen content of nitrate % | Sample | Length of weathering in months | Nitrogen content of nitrate % |
|---|---|---|---|---|---|
| [b]$Y_{3-O}$ | 3 | 11.05 | [d]$Y_{3-D}$ | | 10.91 |
| [b]$Y_{3-O}$ | 3 | 11.04 | [d]$Y_{12-D}$ | | 10.96 |
| [c]$Y_{1-B}$ | 6 | 10.91 | [e]$N_1$ | 3 | 11.06 |
| [c]$Y_{15-B}$ | 6 | 11.14 | [e]$N_{c-1}$ | 3 | 10.96 |

[a]Same technical nitration mixture of $HNO_3$-$H_2SO_4$-$H_2O$ used for all samples.

[b]Stored over conc. $H_2SO_4$ for ten months, then weathered in an open shed.

[c]Stored over conc. $H_2SO_4$ for seven months, then weathered in a basement room.

[d]Stored for first seven months over conc. $H_2SO_4$ and last six months over no drying agent.

[e]Stored in a desiccator for ten months, then weathered in an open shed.

[f]All weathered samples were stored over conc. $H_2SO_4$ for two weeks prior to nitration.

lead tetraacetate oxidation, test runs were made upon an ethyl acetate-acetic acid solution of glycerol and glucose, respectively (with 0.1 normal lead tetraacetate). Exactly the theoretical amounts of the tetraacetate, per mole of the oxidizable substance, were consumed. The ethyl acetate slowly reduced some tetraacetate, but this effect was corrected by a blank oxidation.

Oxidations upon all the nitrocelluloses were performed in duplicate and gave remarkably close checks when the procedure of flushing the pipette, which was used for transferring the solution of nitrocellulose, was adopted. All oxidations of nitrocelluloses were carried out with portions of the same lead tetraacetate solution (approximately 0.107 normal).

To discover whether the lead tetraacetate would hydrolyze or otherwise attack positions protected by nitrate groups, a simultaneous experiment was performed upon a nitrocellulose, sample P, (13.8% N) obtained with the phosphorus pentoxide-nitric acid mixture. The consumption by the nitrate, of approximately 0.01 moles oxidant per glucose unit, remained practically constant and low even after a period of seven hundred hours (Table VII, page 63 and Figure 10, page 95).

Technical nitrocelluloses oxidized with 0.1 N lead tetraacetate for approximately one thousand hours showed continued consumption of the oxidant even after eight hundred hours (Samples $R_0$ to $R_{17}$, Tables VI, XVIII, pages 61 and 93, and Fig. 10, page 95). After four hundred hours,

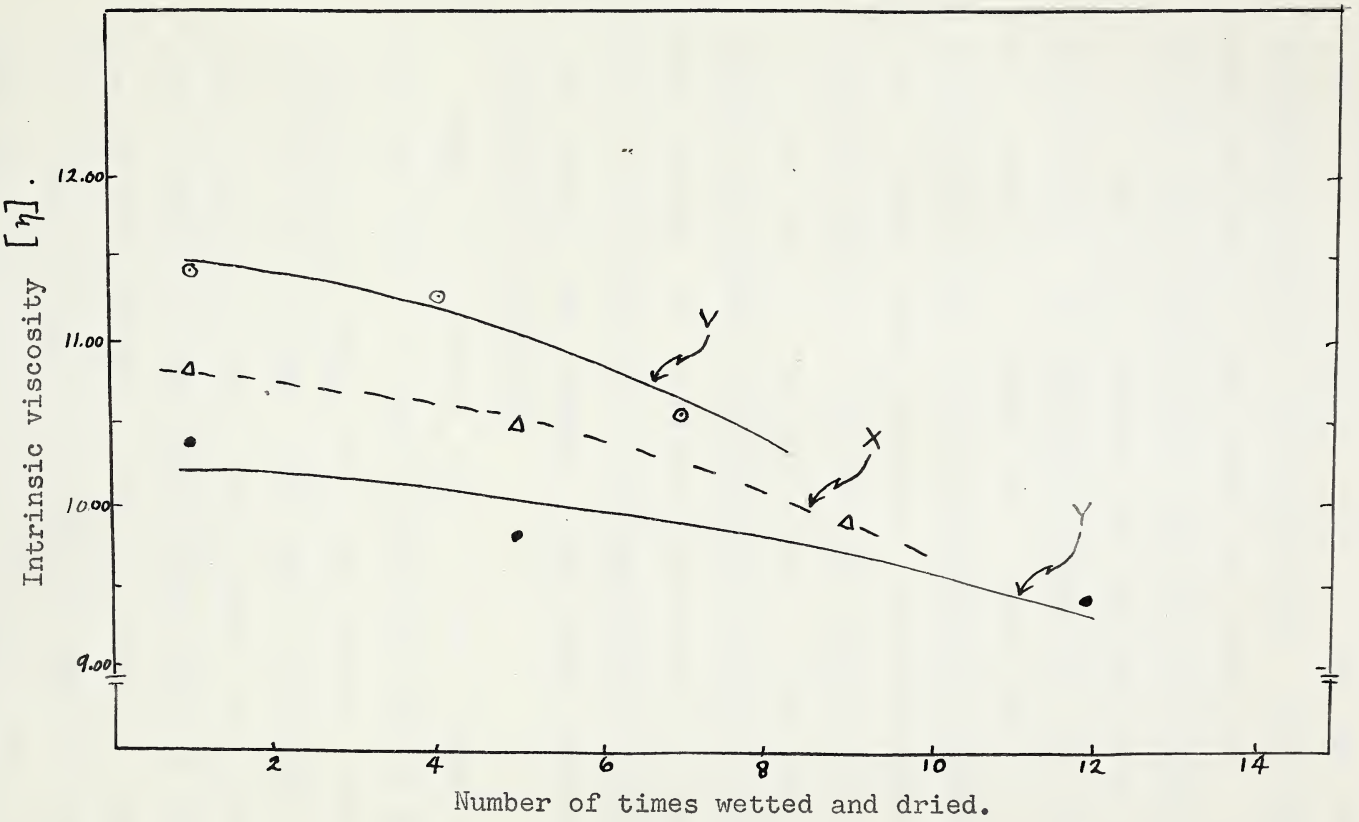



Fig. 9.- Viscosities of cellulose nitrates in butyl acetate.

V ⊙ - Cotton linters dried over $P_2O_5$ under vacuum.
X △ - Dried in air, then over $P_2O_5$ under vacuum.
Y • - Dried in air, then stored over conc. $H_2SO_4$.

it was believed that oxidation of the nitrocellulose, depicted by $R_o$ (Fig. 10) had attained a maximum consumption of lead tetraacetate. Thus, it was taken out of the bath and left at room temperature. Upon rechecking, sometime later, it was found that consumption of oxidant was still taking place, but since the temperature had not been kept constant, the remainder of the plot is not shown. The remaining Samples, $R_1$, $R_5$, and $R_{17}$, were accordingly oxidized for a longer period of time. Considerable error arose in pipetting the nitrocellulose solutions during the first one hundred hours of oxidation because of the fact that solutions of nitrocelluloses having a higher nitrogen content, were more viscous than those of nitrocelluloses with a lower per cent nitrogen. To eliminate this error, the pipette was, for the remainder of the experiments, flushed with ethyl acetate, the flushing liquid being added to the solution to be titrated.

Table VIII and XIX, pages 64 and 97 respectively, show the results of similar oxidations carried out upon nitrocelluloses (Sample S) having nitrogen content ranging from 9.46 to 9.94%. Here again a continual consumption of oxidant by the nitrocelluloses was observed even after a period of four hundred hours (Fig. 11 and 12). The cotton linters used in the preparation of nitrocellulose samples S were part of the same swollen linters which were used previously in the preparation of nitro-

TABLE XVll

NITRATIONS OF COTTON LINTERS GIVEN PROLONGED SOAKING IN DISTILLED WATER

| Sample | Treatment prior[a] to Nitration | Extent of nitration % |
|---|---|---|
| $A_1$ | One water immersion of 17 days. Air dried. | 10.96 |
| $A_2$ | A second immersion of 30 days. Air dried. | 11.02 |
| $B_o$ | No immersion in water. Air dried. | 11.04 |
| $B_1$ | One water immersion of 17 days. Dried over $P_2O_5$ under vacuum. | 11.02 |
| $B_2$ | A second immersion of 30 days. Drying as for $B_1$. | 10.98 |

[a]All samples treated as indicated and then stored over conc. $H_2SO_4$ before nitration.

TABLE XVIII

LEAD TETRAACETATE OXIDATIONS[a] OF TECHNICAL NITROCELLULOSES

| Sample | No. of times soaked and dried[b] | Nitrogen[c] content of nitrate % | Consumption of oxidant moles$\times 10^{-2}$ per glucose unit at 250 hours | Consumption of oxidant moles $\times 10^{-2}$ per glucose unit at 800 hours |
|---|---|---|---|---|
| $R_o$ | 0 | ---- | 11.4 | --- |
| $R_1$ | 1 | 11.09 | 10.4 | 19.6 |
| $R_5$ | 5 | 11.15 | 9.3 | 19.2 |
| $R_{17}$ | 17 | 11.36 | 7.4 | 16.9 |

[a] 0.1 normal $Pb(OAc)_4$ used as oxidizing agent. In ethyl acetate at $25^{\circ} \pm 0.01^{\circ}$.

[b] Dry sample soaked in water and dried in air. Samples stored over conc. $H_2SO_4$.

[c] Average of duplicate or triplicate estimations agreeing within $\pm 0.05\%$.

[d] Cotton linters nitrated with $HNO_3$-$H_2SO_4$-$H_2O$ mixture.

cellulose Samples R (Table XVIII, page 93 ). $S_o$ and $S_{10}$ were nitrated at the same time and under identical conditions. Similarily $S_1$ and $S_{17}$ were nitrated under identical conditions but differing, in time and temperature only, from those used in the preparation of $S_o$ and $S_{10}$.

An attempt was made to oxidize nitrocelluloses, of 7.0% nitrogen content, in ethyl acetate, but this was abandoned due to the insolubility of the mononitrate in the solvent.

With reference to all work involving oxidation of nitrocelluloses, it might be said that lead tetraacetate oxidations, carried out under conditions as described in this thesis, failed to reveal data which might be used to indicate any preferential esterification of the glucose unit (since no curve depicted in Figs. 10, 11, 12, had attained zero slope). Brown and Purves (63) also found that most of their purified nitrocelluloses showed a continuous consumption of oxidant even after a period of three hundred hours. However, nitrocelluloses obtained from cotton linters which were alternately wetted and dried seventeen times consumed less oxidant than the nitrocelluloses obtained from cotton linters which were wetted and dried only once (Fig. 10, page 95, and Fig. 11, page 98 ). As consumption of oxidant by a nitrocellulose should decrease with increased degree

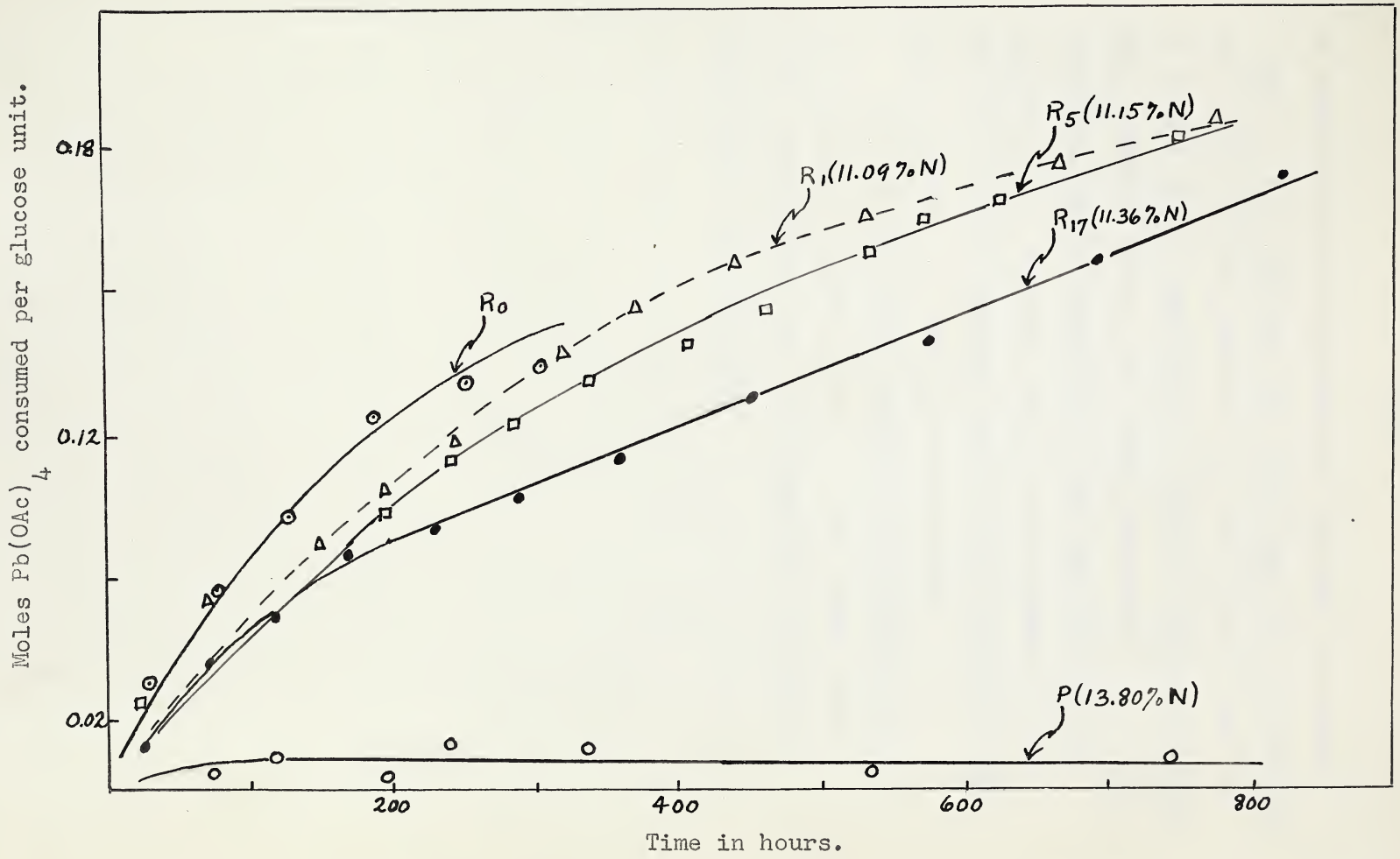



Fig. 10.-Lead tetraacetate oxidations of nitrocelluloses in ethyl acetate-acetic acid.

of substitution of the secondary hydroxyls on carbons 2 and 3, it is apparent that there were more unsubstituted ∝ glycols in $R_1$ than in $R_{17}$ and similarily more in $S_1$ than in $S_{17}$. Therefore, it might be said that seventeen cyclical wetting and drying treatments led to an increased ease of nitration of the hydroxyls in the glycol group. However, there is no evidence to show that the primary hydroxyl has not been similarily made more accessible by wetting drying cycles.

All of the results support the hypothesis that the previous moisture history of the cotton linters plays an important role in influencing the ease of nitration of the cellulose.

TABLE XIX

LEAD TETRAACETATE OXIDATIONS OF TECHNICAL NITROCELLULOSES[b]

| Sample[a] | No. of times soaked and dried[c] | Nitrogen content of nitrate % | Consumption of oxidant in moles $\times 10^{-2}$ per glucose unit after 400 hours |
|---|---|---|---|
| S 0 | 0 | 9.72 | 25.4 |
| S 10 | 10 | 9.94 | 23.8 |
| S 1 | 1 | 9.46 | 29.4 |
| S 17 | 17 | 9.92 | 26.3 |

[a] S 0 and S 10 nitrated under identical conditions. S 1 and S 17 nitrated under identical conditions but different from those used for S 0 and S 10.

[b] Nitrocelluloses were only partially soluble in ethyl acetate. S 0 and S 10 was shaken in ethyl acetate, prior to oxidation, for a different length of time, than S 1 and S 17.

[c] Same swollen cellulose used as indicated in Table XV.

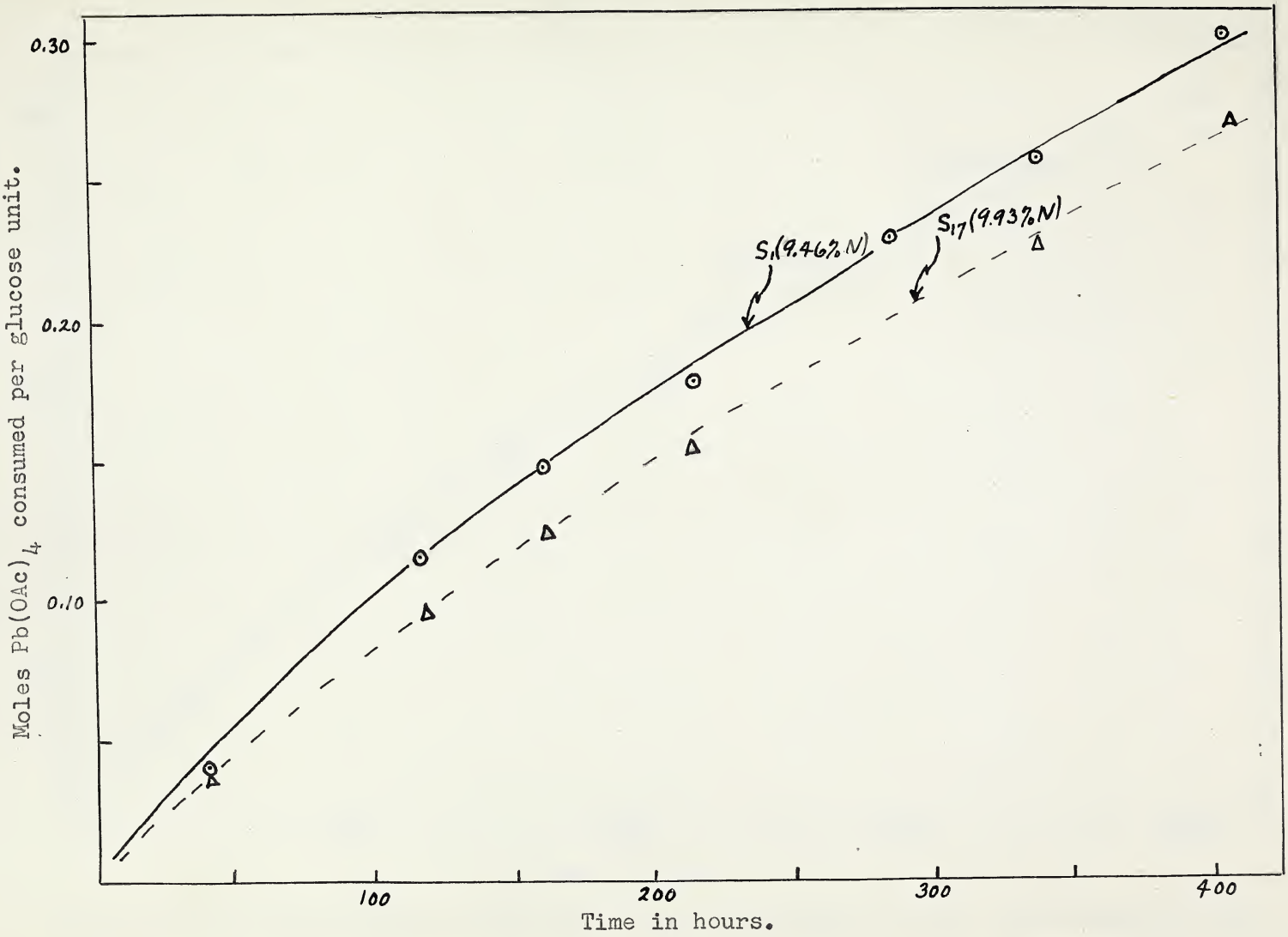



Fig. 11.-Lead tetraacetate oxidations of nitrocelluloses in ethyl acetate-acetic acid.

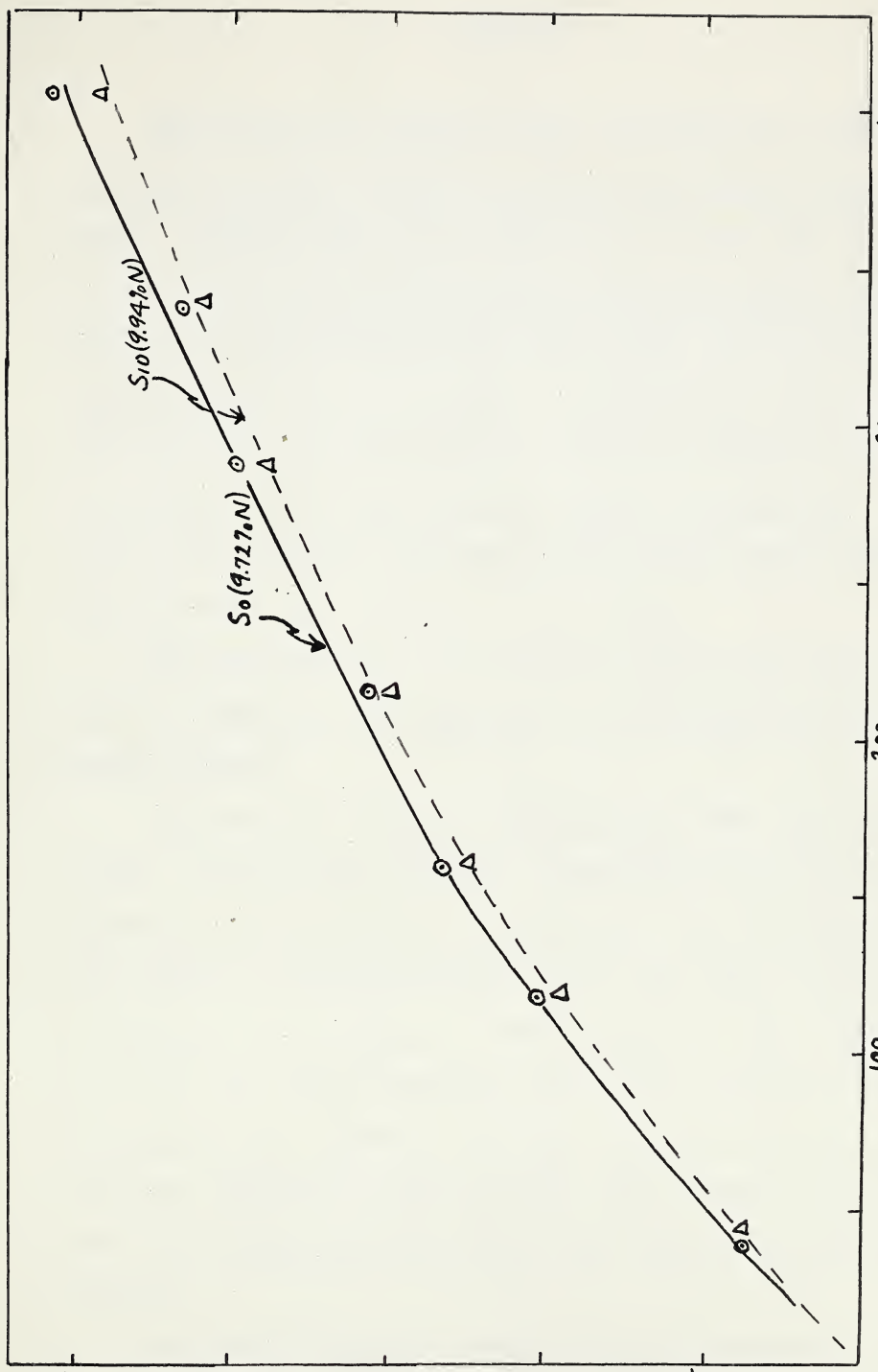



Fig. 12.-Lead tetraacetate oxidations of nitrocelluloses in ethyl acetate-acetic acid.

## SUMMARY

Quantities of dewaxed cotton linters were given as many as seventeen alternate wetting and drying treatments. Drying after each immersion in water was achieved either in air or over phosphoric anhydride under vacuum. Samples of the dried linters were taken after each wetting-drying cycle and stored in a desiccator either over concentrated sulphuric acid or without a drying agent. Measurements of accessibility, degree of nitration, viscosity of the nitrates, and lead tetraacetate oxidations of the nitrates were made upon each sample.

The accessibility to thallous ethylate in ether was found to increase with increase in the number of wetting-drying cycles.

Improvement in degree of nitration with each of a series of nitrating mixtures, calculated to give nitrogen contents of from seven to fourteen per cent, paralleled the number of wetting-drying cycles and apparently reached a maximum in the region of twelve cycles. The increase of nitration was more pronounced with those samples more sharply dried. Repeated nitrogen analyses indicated that the more vigorously dried linters gave nitrates of somewhat more heterogeneous nature than those from air-dried linters.

Prolonged immersion of thirty days in water had no

more effect upon linters than a three-hour immersion.

Exposure of samples of wetted and dried linters to atmospheric conditions in an open, unheated shed from December to March, or in a basement room for six months, largely eliminated the difference in degree of nitration previously possible but also tended to yield a nitrate of somewhat higher nitrogen content than obtained from the original untreated, dewaxed linters.

The intrinsic viscosities of the nitrates in butyl acetate decreased as the number of wetting-drying cycles increased in spite of the parallel increase in per cent nitrogen.

There was a progressive decrease in the consumption of lead tetraacetate oxidant by cellulose nitrate solutions with the increase in the number of alternate wetting-drying treatments of the original linters, but all nitrates investigated showed consumption of oxidant even after a period of nine hundred hours.

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